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AMMRC CTR 77-18

A SURVEY OF THE USE OF CERAMICS IN BATTERY AND FUEL CELL APPLICATIONS

June 1977

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Final Report Contract Number DAAG46-77-M-0460

Approved for public release; distribution unlimited.

Prepared for

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02171

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AMMRC CTR-77-18

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): A Survey of The Use of Ceramics in Battery and Fuel Cell Applications.

5. TYPE OF REPORT & PERIOD COVERED: Final Report (Jan-Jun 1977)

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): Eric W. Brooman, Keith R. Shillito [redacted] Walter K. Boyd

8. CONTRACT OR GRANT NUMBER(s): DAAG46-77-M-0460

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Battelle's Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: D/A Project: 1T162105AH84; AMCMS Code: 612105.11.H8400; Agency Accession: DA OE4741

11. CONTROLLING OFFICE NAME AND ADDRESS: Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172

12. REPORT DATE: June 1977

13. NUMBER OF PAGES: 86

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

407 080

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Battery
Ceramic Materials
Solid Electrolytes
Fuel Cell

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A survey has been carried out examining the use of ceramics in battery and fuel cell applications. Brief descriptions and characteristics of batteries are presented, including those operating at near ambient and at elevated temperatures. The current technology of fuel cells is also discussed. Finally, a detailed analysis of the problem areas and related research needs for ceramics in these applications is provided together with recommendations for future work in this area.

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ABSTRACT

A survey has been carried out examining the use of ceramics in battery and fuel cell applications. Brief descriptions and characteristics of batteries are presented, including those operating at near ambient and at elevated temperatures. The current technology of fuel cells is also discussed. Finally, a detailed analysis of the problem areas and research needs for ceramics in these applications is provided, together with recommendations for future work in this area.

PREFACE

Contract DAAG46-77-M-0460 with Battelle's Columbus Laboratories, Columbus, Ohio was sponsored by the Army Materials and Mechanics Research Center, Watertown, Massachusetts, and was administered under the technical direction of Dr. James W. McCauley of the Ceramics Research Division, AMMRC. Special assitance from Drs. D. J. Viechnicki, H. Priest, W. J. Croft, M. Alexander and P. Sagalyn (AMMRC) is acknowledged.

INTRODUCTION

The U.S. Army needs power supplies (batteries and fuel cells) for a wide variety of applications. Consequently, many agencies are involved with their procurement, or improvement through various RD&D activities. To meet new duty requirements, radical advances in technology including new systems, must be promoted. In addition, in the private industry sector, many companies are working on advanced concept batteries and fuel cells for eventual commercialization and/or use in the military services. Ceramic materials play an important role in many of the battery and fuel cell concepts in use and under development, whether as solid electrolytes, electrical insulators, or separators, for example. Unfortunately, there is no comprehensive review of the state of the art of this rapidly emerging technology, and the dependence on ceramic materials often is not fully appreciated. Similarly, there is no broad overview available of the research needs for ceramic materials improvement. Recognizing this, the Army Materials and Mechanics Research Center recommended that the present study be funded to serve as a datum point with which to compare proposed ceramics needs, and upon which to build a coordinated effort in this area of electrochemical power sources.

Technical Objectives

The technical objectives of the program were (1) to survey current technology in the area of ceramics used for battery and fuel cell applications, and (2) to provide the Army Materials and Mechanics Research Center with identified research needs associated with the use of ceramics in batteries and fuel cells.

Technical Approach

The overall program was divided into two tasks. A critical survey of current technology constituted Task 1. The use of ceramics as electrical insulators, structural materials, separators and solid electrolytes was considered. Individual battery systems were studied, and reference made to associated technology in fuel cells and water electrolyzers. Similarities and differences between the various applications and their requirements were considered. In Task 2 the research needs were identified using the data base generated, supplemented by personal contact with researchers active in this general area of technology. Needs were related to both materials problems and electrochemical problems.

While Tasks 1 and 2 have been described separately above, to some extent they are interrelated, and efforts on these tasks were carried out concurrently to a large degree. Task 2, however, was dependent upon the completeness of the survey made under Task 1.

In performing the Task 1 survey, experience gained through prior contracts on surveying the available and required technology for bulk electrical energy storage, and on developing primary and secondary battery systems and fuel cells for a wide range of applications, formed a base upon which to build. The availability of the Electrochemical Energy Storage Index, the Battery Information Index, and the Battelle information resources supplemented the data base. Attendance by BCL electrochemists and ceramists at several national meetings of engineering societies also added to the information resources. Finally, personal contact with researchers active in the development of ceramic materials for battery and fuel cell applications ensured the comprehensiveness and timeliness of the material needed to complete the survey.

In determining research needs in Task 2, it became apparent that some materials were common to a variety of individual battery systems, and also the performance of some ceramic materials in certain functions was acceptable, compared with the need for improvement in other functions. Thus many of the identified research needs concern separator materials and solid electrolyte materials, which directly affect the performance of the electrochemical devices. Less emphasis has been placed on ceramic materials used for feedthroughs, for example, because these only indirectly affect performance, and in low temperature devices have usually proved to be reliable in service.

TECHNICAL SUMMARY

The use of ceramic materials in primary, secondary, thermal and reserve batteries; and in fuel cells having aqueous, molten salt or solid electrolytes is described. Application of these materials is mainly found as (1) Separator, spacer or matrix components, (2) Solid electrolyte components, and (3) Seals and feedthrough (electrical insulation) components. Other uses are as miscellaneous structural materials and electrode support materials, as thermal insulation, as corrosion-resistant coatings, and as electrolyte additives.

Asbestos, fiber glass mats, boron nitride mats/cloth, and zirconia cloth are the principal separator materials in use in batteries. Beta-alumina or sodium-ion conducting glasses are the principal solid electrolyte materials. Glasses, alpha-alumina, beryllia and boron nitride are the most common electrically insulating materials used in feedthroughs and seals. In low temperature fuel cells, asbestos and potassium titanate have been used as separator/matrix materials, while doped zirconia, thoria or ceria have been used as solid electrolytes at elevated temperature. Transition metal oxides and carbides have been used as electrocatalysts, as have various perovskite-type materials. Glasses and alpha-alumina are used mainly for seals and feedthroughs.

Problem areas have been identified for both batteries and fuel cells, and approaches to resolving these problems through the use of ceramic materials are discussed. Research needs have been delineated. With the majority of battery and fuel cell systems, emphasis is on developing practical commercial hardware, or devices for use by the DoD. There is, however, a real need for two types of supportive effort, both involving R&D as opposed to engineering development. The first effort includes general studies to improve materials properties such as toughness and strength, and stability such that processing technology can be advanced to the stage that low cost components can be fabricated. The second effort is of a more theoretical nature and should address such problems as developing an understanding of structure/conductivity relationships in solid electrolytes, and

an understanding of the mechanisms of degradation and corrosion attack. The role of impurities, both in the ceramic materials themselves, or leached from other cell components, is likely to assume increasing importance as more efficient and longer-lived devices are required.

DETAILED PROGRAM FINDINGS

Scope and Terminology

During the Task 1 studies the scope was purposely kept as wide as possible to reflect the very many applications for ceramic materials. The following systems were considered:

- Primary Batteries (non-rechargeable)
- Reserve Batteries (activated just prior to use)
- Secondary Batteries (rechargeable)
- High Temperature, Advanced Batteries (rechargeable)
- Thermal Batteries (non-rechargeable)
- Low Temperature Fuel Cells (aqueous electrolytes)
- High Temperature Fuel Cells (liquid, solid electrolytes)
- Fuel Processors (for fuel cells)
- Water Electrolyzers (for producing hydrogen fuel)

and supporting equipment where appropriate. In analyzing the requirements for these systems it was convenient to categorize the use of ceramic materials according to the following classification:

- Electrodes (electronic conductors)
- Electrolytes (ionic conductors)
- Separators and Spacers (electrical insulators)
- Seals (mechanical function)
- Feedthroughs (electrical function)
- Coatings and Structural Components

where, in general, the usual electrochemical (battery or fuel cell) terminology is implied. Under the "electrode" category the ceramic materials may either function as the active electrode material itself, or as a support for the electrochemically active material, as is often found in fuel cells.

In "electrolytes", again the ceramic material may either act as the ionic conductor, as in sodium-sulfur batteries, or it may be present as an immobilizer as in some "non-spill" lead-acid batteries. "Separators" may be either solid or porous ceramic materials, powder materials, fibrous materials (non-woven fabrics) or incorporated into other organic or inorganic materials as fillers. "Spacers" are inert materials which serve to fill voids in the internal volume of devices in order to reduce electrolyte requirements, or to prevent excessive vibrations, for example. One or more terminals, usually on a battery, are insulated from the cell case if it is an electrical conductor. "Feedthroughs" are needed to accomplish this, and these are usually of a ceramic-to-metal type. Ordinary cell closures, or joints between internal cell components may not need to be electrical insulators. These closures are referred as "seals", and may have the same requirements as "feedthroughs" in some instances to provide hermeticity. Ceramic coatings may be used on container materials or current collectors to impart corrosion resistance. Finally, ceramic materials may be used primarily as structural members, for example stiffener plates in battery assemblies.

In the Task 1 studies the term ceramic was used somewhat loosely to include conventional ceramic materials, such as refractories, porcelains and glasses, as well as ceramic-like inorganic materials, such as borides and nitrides, and asbestos. A limited discussion is included in this report about these ceramic-like materials because of the similarity in requirements, properties and applications with many of the ceramic materials identified.

For the purposes of this study it is convenient to think of batteries which operate at near ambient temperatures, (-40 to +75C) and those that oeprate at elevated temperature (∿200 to 450C). Under the former category fall most conventional batteries of the primary, reserve and secondary types which are relatively well developed, and are manufactured commercially. The type of construction and materials employed are usually well known, and the cells and batteries well characterized, physically, chemically and electrically. High temperature batteries refer to secondary batteries with the potential for delivering large amounts of power; and storing relatively large amounts of energy in hardware of smaller volume than the low (ambient) temperature batteries. The high-temperature batteries are often referred to as "advanced" batteries, and they are relatively less developed. Batteries often have not been evaluated, although cells have been characterized in the laboratory. Thermal batteries are usually primary batteries of the reserve type, which are activated by causing one or more of the cell active components to melt at the elevated temperatures generated.

Batteries Which Operate at Near Ambient Temperature

Table 1 summarizes the data obtained during the survey of cells or batteries which operate at near ambient temperatures. A general discussion about the specific uses of these ceramic materials follows the detailed review of both high-temperature batteries and low-temperature types. Problem areas are discussed in more detail in a subsequent section of this report prior to identifying research needs.

Lithium - Thionyl Chloride Batteries

Lithium - thionyl chloride cells and batteries have become available in reasonable quantities during the last few years, and are a relatively recent addition to the high energy density systems operable at ambient temperature. This type of cell is being evaluated for application in the U.S. Air Force(1), Navy(2) and Army(3), for example, and companies such as EIC Corporation, GTE Laboratories, Inc., Honeywell, Inc., and P. R. Mallory and Company, Inc., are involved in their research, development and commercialization. D - size, cylindrical cells are common, but work is proceeding on the development of prismatic cells of up to 4000 ampere hour capacity(1).

Pre-assembled, glass-to-metal seals have been found to be the only type satisfactory for hermetic feedthroughs(4) for this type of cell. Polymeric materials for crimped seals were found to be subject to cold flow, and also to chemical degradation by the highly oxidizing conditions found in these cells due to the reactivity of the active materials(6). Figure 1 shows the type of glass-to-metal seal which has been successfully used as a feedthrough for low-rate cells used in such sensitive applications as medically inplanted devices(4). However, because of problems experienced with some cells under high-rate operating conditions, a safety vent can be

Table 1. Uses of Ceramic Materials in Batteries Which Operate at Near Ambient Temperatures

Battery System	Type of Battery	Electrodes	Electrolytes	Spacers and Separators	Seals	Feedthroughs	Coatings and Structural Components
(1) Lithium-Thionyl Chloride	Primary	--	--	Borosilicate Glasses	--	Glass-to-Metal	--
(2) Lithium-Vanadium Pentoxide	Primary	--	--	--	--	Glass-to-Metal	--
(3) Zinc-Mercuric Oxide	Primary	(TiO_2)	(SiO_2)	--	--	Ceramic-to-Metal	--
(4) Zinc-Silver Oxide	Reserve	--	--	Asbestos	--	--	--
(5) Zinc-Silver Oxide	Primary and Secondary	(TiO_2)	(SiO_2)	Pressed and Sintered Ceramic Powders	--	--	Epoxy-Fiber Glass Stiffeners
(6) Zinc-Oxygen(air)	Secondary	--	--	Asbestos	--	--	--
(7) Hydrogen-Silver Oxide	Secondary	--	--	Asbestos: Asbestos + Plastic + Ceramic	--	--	--
(8) Hydrogen-Nickel Hydroxide	Secondary	--	--	Asbestos: Potassium Titanate	--	--	--
(9) Cadmium-Nickel Hydroxide	Secondary	--	--	--	--	Ceramic-to-Metal	--
(10) Lead-Lead Dioxide (Lead-Acid)	Secondary	(TiO_2) (Al_2O_3) (SiO_2)	(SiO_2)	Silica + Polyethylene: Fiber Glass Cloth	--	--	--
(11) Sodium-Bromine	Primary	--	Beta-Alumina	--	Glass	--	--
(12) Lithium-Iodine	Primary	--	--	Steatite: Fiber Glass Reinforced Polyester	--	?	--

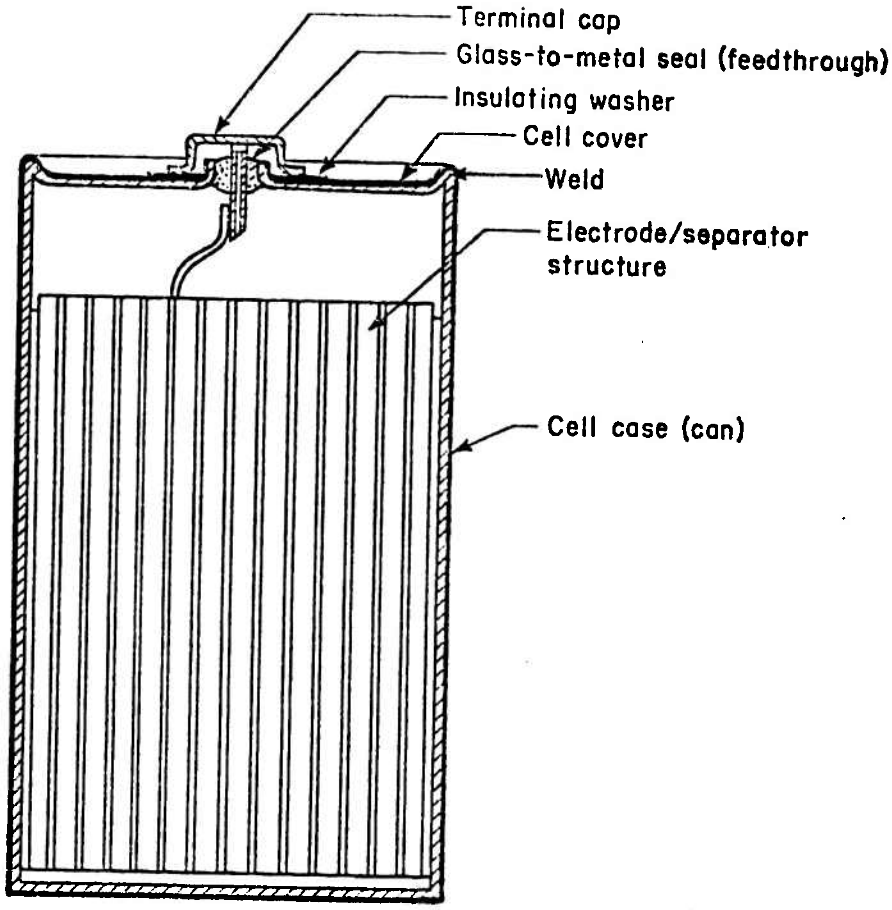

FIGURE 1. SCHEMATIC REPRESENTATION OF ONE TYPE OF GLASS-TO-METAL HERMETIC SEAL ARRANGEMENT IN LITHIUM-THIONYL CHLORIDE D-SIZE CELLS.

incorporated to relieve internal gas pressure build up, and to minimize the risk of thermal runaway[5].

Various borosilicate glasses have been investigated[6] for use in seals and as separator materials to withstand the oxidizing environment within the cells. These materials were found to be stable in the tests performed. The only observable effect of exposure to 1-8 M $LiAlCl_4/SOC\ell_2$ solutions was a partial exchange of lithium ions with the cations at the surface of the glass in contact with the test solution. It was concluded that borosilicate glasses are useful separator materials for lithium-thionyl chloride cells.

Lithium - Vanadium Pentoxide Batteries

Primary active and reserve batteries of this type are under development[7] and being evaluated[8] because of their high-energy density and high-cell voltage ($\sim$3·5v). Reserve cells built by Honeywell Power Service Center[7] incorporate a glass-to-metal seal between the stainless steel case (electrically connected to the positive electrode) and the negative terminal. Few details of the seal are given in the scientific literature, but additional information is available from Honeywell, who are under contract to Picatinny Arsenal and the Army ECOM to perform certain phases of the development work. Figure 2, taken from Reference (9) depicts the type of glass-to-metal seal arrangement used on reserve cells with design capacities of 0.100, 0.185, and 0.500 ampere hour.

Zinc - Mercuric Oxide Batteries

This is an alkaline electrolyte battery system which has been available for many years in cylindrical configurations. Conventional zinc - mercuric oxide batteries do not contain ceramic materials, and suffer from several shortcomings when operated at low-current drains for extended periods of time. For example, internal shorts may develop, there may be electrolyte leakage, self-discharge and the development of high-contact impedance. For certain applications, such as their use in implantable cardiac pulse generators, these shortcomings must be overcome if a satisfactory product is to be marketed. The Medical Systems Division of the General Electric Company have developed reliable, long-life zinc - mercuric oxide cells which

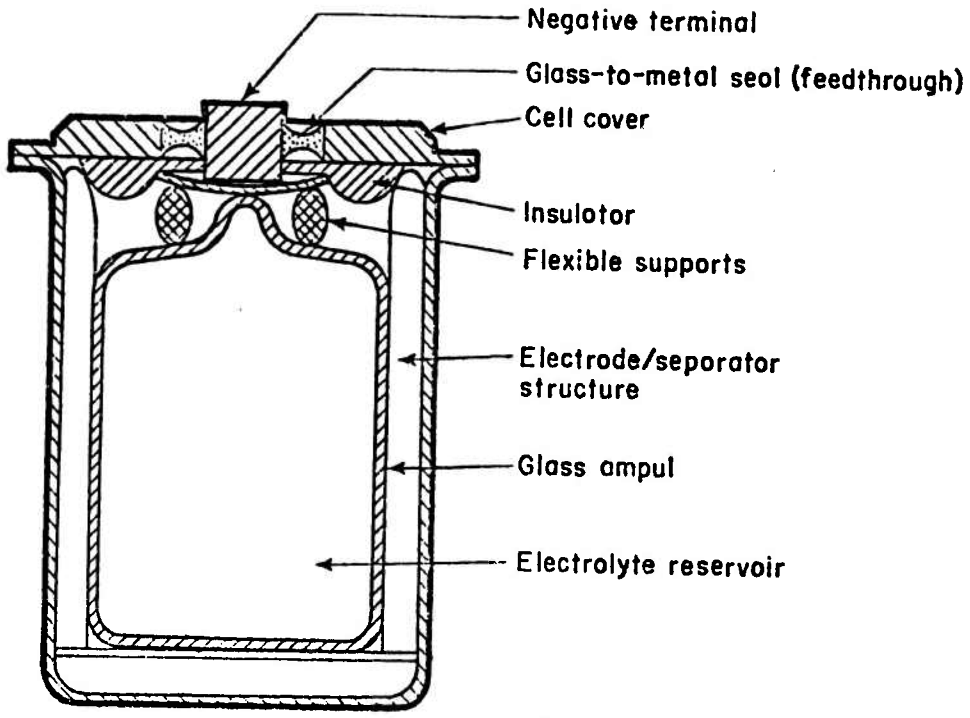

FIGURE 2. SCHEMATIC REPRESENTATION OF THE GLASS-TO-METAL SEAL ARRANGEMENT ON RESERVE LITHIUM-VANADIUM PENTOXIDE CELLS.

do not exhibit the problems described above[10]. These cells incorporate a ceramic-to-metal seal as a feedthrough. This seal is of the aerospace type incorporating an alumina-based ceramic insert brazed to the negative terminal post, and provides a hermetic closure.

Zinc - Silver Oxide Batteries

Secondary silver - zinc cells have been developed for aerospace operations, one of the requirements for which is that the cells must be sterilizable. Sterilization at 145 C imposes severe requirements for separator (and other organic) materials which are commonly used for terrestrial applications. The Astropower Laboratory of Douglas Aircraft Company, developed some time ago[11] a proprietary ceramic separator material capable of withstanding chemical attack by the hot KOH electrolyte. The ceramic materials (not identified) in the form of a powder, were milled with a binder, pressed in a die, then sintered to form permeable discs or sheets for use in experimental cells evaluated under contract to NASA Lewis Research Center[12].

A secondary silver - zinc battery has also been described in the literature[13] in which cells are assembled with stiffening plates of epoxy-fiber glass composition prior to being encapsulated and assembled into the battery pack. The purpose of these stiffeners was to transmit the high-g entry loads to the case walls, rather than directly through the Eagle-Picher cells manufactured for this Venus Probe battery.

In a patent assigned to ESB Incorporated[14] zinc electrodes containing titanium dioxide are said to give relatively high discharge rates and to improve the shelf life of primary, alkaline zinc - mercuric oxide and zinc - silver oxide cells. The patent describes the performance of these batteries. In an earlier patent to ESB Incorporated[15] silicon and silicate additions to the alkaline electrolytes of such cells were also said to improve the capacity and impart increased stability during storage. The present status of these developments is not known.

Finally, as Table 1 indicates, reserve silver - zinc cells have been fabricated which incorporate fuel cell-grade asbestos materials as separators. These reserve cells were built by Eagle-Picher Industries for the U.S. Air Force under a contract (F04701-73-C-02010) awarded in 1973.

Zinc - Oxygen (Air) Batteries

Primary zinc - air cells and secondary zinc - air batteries have been under development since the mid-1960's, and have received attention for military application because the oxidant need not be incorporated in the battery-active material, thus saving weight. The secondary types can be either electrically or mechanically recharged. One type of electrically rechargeable battery with a recirculating electrolyte system is known to utilize asbestos separator materials[(16)]. A concentric tubular electrode design is described with the asbestor separator being about 0.3 mm thick. The selection of the materials used in this type of battery was based upon the premises of, (1) ease of fabrication, (2) low cost, and (3) proven long life under the design operating conditions, e.g., operation at 50 to 55 C. The tubular design was chosen to optimize the hydrodynamics of the system, which in turn affect the electrochemical performance.

Hydrogen - Silver Oxide or Nickel Hydroxide Batteries

These are a relatively recent development among secondary batteries directed towards eventual aerospace or military applications. The proven performance of the nickel hydroxide- or silver oxide electrodes is coupled with the efficient operation of the hydrogen electrode, developed previously on fuel cell R&D programs. Coupling these systems circumvents the problems with cadmium and zinc electrodes in the more conventional zinc - silver oxide, and cadmium - nickel hydroxide cells. However, as presently configured, these metal - hydrogen batteries must be enclosed in a pressure vessel to contain the pressurized hydrogen, or the hydrogen must be stored in a metallic hydride system to be developed. A description of these systems is given in References (17) and (18).

In a discussion of the life-testing of silver - hydrogen cells[(19)] it was disclosed that a fuel cell-grade asbestos absorber (manufactured by Johns-Manville) and an "Astropower" separator (available through Yardney) were used in the separator system, as shown in Figure 3. The asbestos was about 10 to 12 mils thick, while the "Astropower" separator is a proprietary combination of asbestos, plastic, and ceramic materials, which apparently

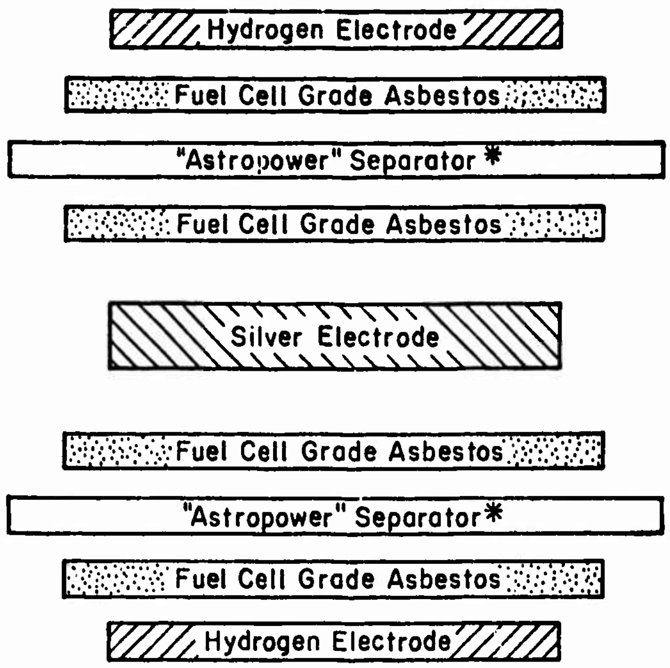

FIGURE 3. DIAGRAM OF A HYDROGEN-SILVER OXIDE ELECTRODE/SEPARATOR STACK CONFIGURATION

had previously been evaluated in silver - zinc cells for NASA. In the silver - zinc cells, the separator was reported to have lasted for 5 or 6 years[19].

In other work performed for the U.S. Air Force, concerning failure mechanisms in nickel - hydrogen cells, the use of fuel cell grade asbestos as a separator material was also mentioned by a representative of EIC Corporation[20]. Work was performed on experimental cells in the laboratory in order to improve upon oxygen and electrolyte management in these type of cells. Electrolyte is lost from the electrode/separator stack by displacement, and it was shown that the asbestos separator, when used, competed with the nickel hydroxide in terms of retaining the electrolyte. In other words, in terms of electrolyte loss the nickel hydroxide electrodes and the asbestos separators behave similarly. Potassium titanate has also been studied as a separator material in cells[25] by the Energy Research Corporation. Second generation 50 ampere hour cells incorporating this separator material have shown encouraging results in life cycle tests.

Cadmium - Nickel Hydroxide Batteries

The nickel hydroxide positive electrode, coupled with an hydrogen electrode above, or in this instance with a cadmium negative electrode, is in reality a hydrated nickel oxide electrode represented by NiOOH. Often this battery system is referred to as the nickel - cadmium battery system, and it has been the mainstay of aerospace programs for the last decade or so, with development funded principally by NASA and the U.S. Air Force. More recently it has found application as a small rechargeable battery for portable devices and appliances.

For the aerospace applications the cells have to be hermetically sealed, and ceramic-to-metal feedthroughs for one or both electrodes have been developed which are found to be satisfactory. Earlier glass-to-metal seals had been used, but the glasses were attacked by the strong alkaline (KOH) solution inside the cell or electrolyte[21]. Of the ceramic materials investigated in the past, 96-percent alumina was chosen for the greatest alkali resistance. Problems with early ceramic-to-metal seals were associated with the brazing materials used to bond the sensitized ceramic to the metal feedthrough terminal. Silver brazing alloys were substitued for the orgininally used gold-nickel brazing alloy because of their greater ductility. However, corrosion of the silver brazes resulted in internal shorting of the cells. Nonproprietary brazing alloys have been developed by General Electric Company, for example, which no longer are subject to the silver migration problem[22].

Reference (23) reports the failure (cracking) of the ceramic material in strenuous vibration tests in the laboratory. In actual flight, however, this type of failure has not been observed. It should also be mentioned that in the vibration tests, failure of the ceramic in the feedthrough was ranked fourth in the frequency of occurrences, below the electrode tabs breaking at the comb weld or near the electrodes themselves, and the cell cover breaking around the terminal.

Eagle-Picher Industries have described[24] new concepts for an advanced, sealed nickel - cadmium cell. In one configuration a fuel cell-grade asbestos mat separator is used, drawing upon technology developed for nickel - hydrogen cells. From the data obtained in laboratory tests with the various configurations, it was not possible to show the superiority of either the asbestos or the conventional Pellon 2505 (nylon) separator material.

Lead - Lead Dioxide Batteries

These batteries incorporate an acid electrolyte, and the system is traditionally known as the lead-acid system. Lead - acid batteries have been used in vehicular applications since the turn of the century. Although exhibiting relatively low energy and power densities, the active materials are in ample supply, and the batteries are well-developed and relatively inexpensive. The most recent developments have been the introduction of "non-spill" batteries, where electrolyte leakage is prevented by chemical and mechanical means, and the low-maintenance batteries, dubbed as "maintenance-free" because watering is usually not necessary during the life of the battery under normal operating conditions. Lead-acid batteries are now available in a wide range of sizes and shapes, and their performance has been slowly, but steadily, improving over the years.

Some of the "non-spill" cells have a gelled, immobilized electrolyte. Gelling is achieved by the addition of a siliceous material. Amorphous silica has been added to the electrolyte of cells containing electrode grids fabricated from a conventional 6 percent antimony-lead alloy. The addition of the silica was said to increase the resistance of the positive electrode to shedding (loss of active material), while at the same time, improving cycle life and the capacity obtainable on discharge over a certain range of compositions[26]. Silica or titania, or alumina may also be used to dispersion-strengthen the electrode grids, thus permitting the amount of hardening alloying additions to be reduced[27]. Commercial cells incorporating these inert ceramic materials, however, have not been reported in the literature.

Another application of silica in lead - acid batteries has been its incorporation into polymeric separator materials, to produce, for example, microporous polyethylene separators[28]. The material produced, after extracing the plasticizing oil, is tough, flexible, strong, and extremely corrosion resistant. Coupled with the fine pore size, the above advantageous properties mean that very thin separators can be fabricated and used in high-performance cells. Fiberglass spacers and separators have also been used in conventional lead - acid batteries. The separator is made from a fiberglass mat, which may contain an intermediate layer of silica powder, and which may have a latex coating to reduce pore size and inhibit antimony transfer, which poisons the positive electrodes[28]. These separators are also tough and flexible, and often are used adjacent to the positives to prevent shedding, essentially by a mechanical retention action. Used in this role, a more conventional separator material is often incorporated to function as the electronic insulator. Sealed, cylindrical lead-acid cells, a recent innovation being investigated for use by the U.S. Air Force, for example[29], are fabricated with a thin glass mat separator material, which is ideally suited for the spiral-wound configuration of the electrode/separator structure. The sealed construction is made possible by the careful selection of materials and the design. Gates Rubber Company, and General Electric Company offer these cells in a variety of sizes on a commercial basis. The performance data reported to date for these cylindrical cells, have been impressive, and they may be suitable for use as non-cranking batteries on aircraft, for example[30], at a cost savings over the batteries presently being used.

Finally, a minor application of ceramic materials, which is not shown in Table 1 is their use in the special plugs used on some low-maintenance batteries[31]. Essentially, these modified cell plugs incorporate a catalytic device for recombining the oxygen and hydrogen produced during recharging, and a method for returning the water formed back to the cells. With these devices water need not be added as frequently as with conventional batteries. The ceramic material can either be present as a packing material (e.g., glass beads) or as a catalyst support (e.g., alumina).

Sodium - Bromine Batteries

Developed for applications having extremely small power requirements, the sodium - bromine battery is a compact and light-weight, hermetically-sealed device. In the General Electric Company design[32] the anode compartment (containing amalgamated sodium) and the cathode compartment (containing bromine associated with a carbon-felt current collector) is separated by a thin disc or tube of beta-alumina, depending on whether a "button" or cylindrical design is being used. This beta-alumina (of approximate composition $Na_2O.9Al_2O_3$) is connected to the cell cover by means of a glass seal, as shown in Figure 4. The cell is operated in the range of 21 to 50 C (above the freezing point of the sodium amalgam) and when discharging sodium ions are transported through the sodium-ion-conducting beta-alumina where they react with bromine to form sodiumbromide, giving a theoretical voltage of 3.78V. A further discussion about the types of beta-alumina available, and used in cells, is given below when high-temperature batteries are being reviewed.

Lithium - Iodine Batteries

This primary battery system is also designed for long-life, low-drain (microamperes) applications such as cardiac pacemakers, and like the sodium - bromine battery, incorporates a solid electrolyte system (lithium iodide) and a hermetic feedthrough device[33]. Fiber-glass reinforcing panels are incorporated in the design, and steatite spacers are used at the top of some cell designs.

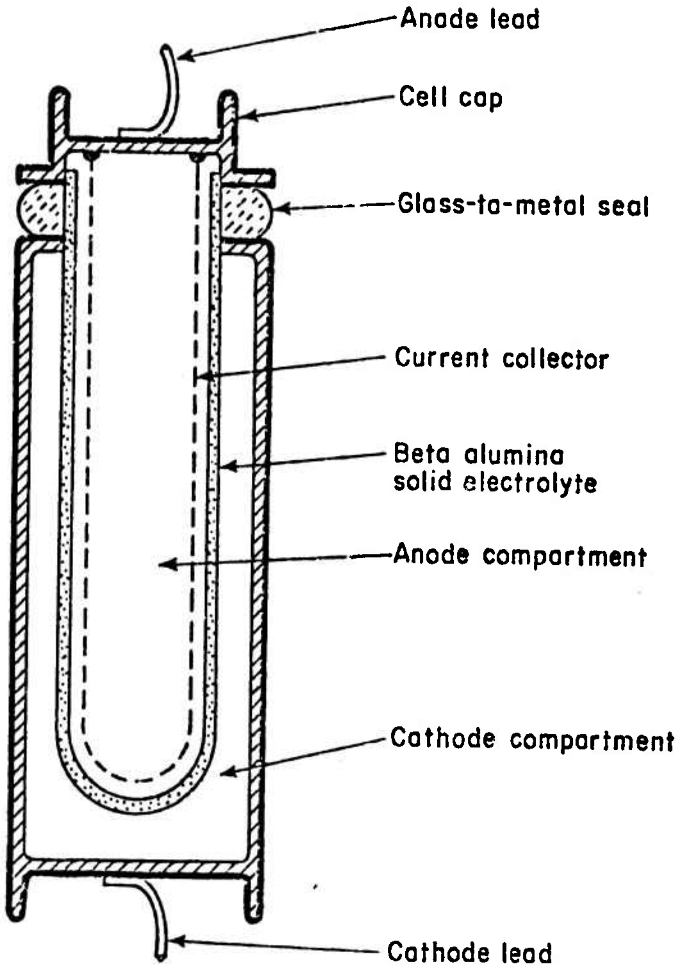

FIGURE 4. SCHEMATIC DIAGRAM OF A CYLINDRICAL SODIUM-BROMINE CELL INCORPORATING A BETA-ALUMINA SOLID ELECTROLYTE

Batteries Operating at Elevated Temperatures

Table 2 summarizes the data obtained during the survey of cells or batteries which operate at elevated temperatures, and a description of the battery systems listed follows. A general discussion of the use of ceramic materials in batteries is given in the next section.

Sodium - Sulfur Batteries

As the name implies, the principal anode reactant is sodium and the cathode reactant is sulfur. At the cell operating temperature, about 300 to 350 C, both these electrode materials are molten. A solid electrolyte is used, which also serves the secondary purpose of separating the anodic and cathodic reactants, thus preventing internal shorting of the cell. The cell configuration is the opposite of conventional batteries which have solid electrdoe materials and a liquid electrolyte.

Sodium - sulfur batteries are being developed by several companies in the U.S. such as Ford Motor Company, General Electric Company, and Dow Chemical Compa. y, for applications in electric vehicle propulsion systems and bulk energy storage devices. The battery design differs for these applications, although the cell design and chemistry remains similar. A general review of the sodium - sulfur battery systems, and the use of ceramics in these batteries, is to be found in References (34) and (35).

All sodium - sulfur batteries rely on a sodium-ion conducting solid electrolyte to permit transfer of the sodium to the sulfur-containing compartment where polysulfides are formed. The Ford Motor Company and General Electric Company both use beta-aluminas, as did TRW Systems Incorporated, before they ceased R&D work in 1976. The latter were developing planar, disc electrolytes[36], while the former companies are using tubular electrolyte designs, which are also favored by foreign developers of this battery system.

The Dow Chemical Company have a different approach and use thousands of hollow, sodium-ion conducting glass fibers in each cell. The fibers are a borate glass which contains proprietary additives and sodium-fluoride, or more recently, sodium - chloride, to supply excess sodium ions[37].

TABLE 2. USES OF CERAMIC MATERIALS IN BATTERIES WHICH OPERATE AT ELEVATED TEMPERATURES

Battery System	Type of Battery	Electrodes	Electrolytes	Separators and Spacers	Seals	Feedthroughs	Coatings and Structural Components
1) Sodium-Sulfur	Secondary	--	Beta-Alumina Na-Conducting Glasses	Alpha-Alumina Glass Fibers	Glasses: Alpha-Alumina	(Glass-to-Metal)	Solder Glass: Doped-TiO_2: Silicon Carbide
2) Sodium-Metal Chloride	Secondary	--	Beta-Alumina	--	Glass-to-Metal	--	Glass Tubes
3) Potassium-Sulfur	Secondary	--	K^+-Conducting Glasses	--	--	--	Solder Glass
4) Lithium-Metal Sulfide	Secondary	--	--	Boron Nitride Al Nitride: Zirconia Cloth: Yttria Magnesia: Si Nitride: Asbestos Paper	--	Boron Nitride Yttria Powder Ceramic-to -Metal: Betyllium Oxide: Alpha Alumina	Boron Nitride: Ti Nitride: Iron Boride
5) Lithium-Metal Chloride	Secondary	--	--	Boron Nitride	--	Boron Nitride	?
6) Lithium-Vanadium Pentoxide	Thermal	--	--	--	--	Glass-to-Metal	Fiberfrax: Asbestos
7) Calcium-Metal Sulfide	Secondary	--	--	Boron Nitride Zirconia Cloth	--	Alpha Alumina	--
8) Calcium-Calcium Chromate	Thermal	--	(Silica)	--	--	Glass-to Metal	Asbestos: Glass Cloth
9) Sodium-Sodium	Thermo-Electric	--	Beta-Alumina	--	--	--	--

The individual fibers are inexpensive to manufacture, but have to be connected to a ceramic "tube sheet" fabricated from solder glass, a B_2O_3/Na_2O system with controlled water content[38], as shown in Figure 5. Because of the large surface area presented by the glass fibers the effective operating current density is only of the order of $2mA/cm^2$, however, the fiber wall thickness has to be very thin ($\sim$10μm compared with a diameter of $\leq$100μm) in order to minimize the internal resistance of the cell (resistivity of the glass is about $5x10^4 \Omega cm$). The thin fibers are subject to cracking, usually near the joint with the tube sheet, or at imperfections in the glass[37]. Thicker walls favor longer cell life, so a trade-off is indicated.

One design of a sodium - sulfur cell incorporating a tubular beta-alumina solid electrolyte is shown in Figure 6, based on data presented in Reference (39). In this configuration there is the need for both glass-to-metal and ceramic-to-ceramic seals because the electrolyte tube is also supported by a tube sheet, in this instance made from alpha-alumina, and because of the need for a sodium reservoir in U.S. designs. There is a volume change between charged and discharged states of the anode. Without the reservoir, a gasketed, mechanical seal is feasible at the top of each cell[40], otherwise a mechanical seal in the center of the cell is too complex (expensive) for practical purposes. For large batteries, one approach being pursued (General Electric Company) is to use a ceramic tube sheet to support individual cell electrolyte tubes, in much the same way the Dow Chemical Company supports its glass tubes (hollow glass fibers sealed at one end). This ceramic tube sheet, or manifold, and the associated glass seals between the ceramic and the electrolyte tubes, have yet to be developed[40].

In most cell designs the highly oxidizing sulfur/polysulfide mixtures (at $\sim$ 350 C) are in contact with the metal cell containers, and corrosion is a severe problem. Organic coatings have not proved to satisfactory. However, doped - TiO_2 coatings have shown promise for current collectors, and cell containers[41]. Consideration is also being given to using the TiO_2 material for the cell container, and cladding or coating this with a metal for an electrically conductive surface. Doping is required to increase the electrical conductivity of the TiO_2, which in conjunction with the metal coating serves as the cell cathode to which electrical contact is mase. A further discussion about this development is given later.

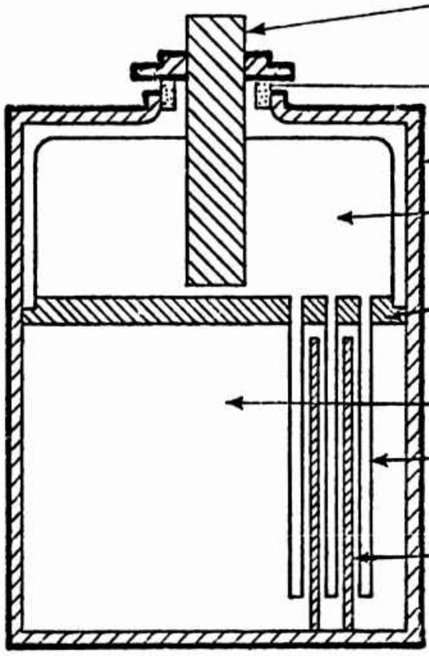

FIGURE 5. SIMPLIFIED DIAGRAM OF THE DOW SODIUM-SULFUR BATTERY SHOWING HOLLOW GLASS FIBERS ATTACHED TO THE CERAMIC TUBE SHEET.

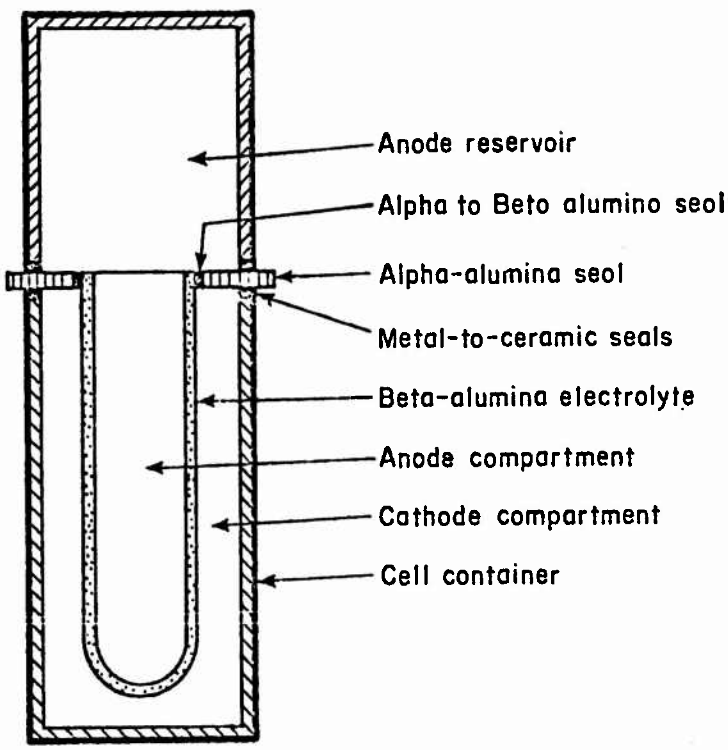

FIGURE 6. REPRESENTATION OF THE FORD SODIUM-SULFUR BATTERY IN ONE OF ITS CONFIGURATIONS

Other approaches to the corrosion problem have revolved around the use of coatings such as silicon carbide, refractory metals or silicon/silicon carbide composites[42] on inexpensive materials such as steel, or light weight materials such as aluminum. Another approach is to use an "inside-out" design in which the sulfur is contained within the electrolyte tube, and the sodium is in contact with the cell container.

Failure of sodium-sulfur batteries is usually the result of the ceramic electrolyte tube cracking, but work is progressing to overcome this problem as outlined later. In some cells a glass fiber sleeve has been placed over the electrolyte tube to prevent sulfur from deposition on the beta-alumina, for example. Controlling electrolyte composition, and limiting impurity levels are other approaches.

Sodium - Metal Chloride Batteries

This system is under development by ESB Incorporated, primarily, for energy storage (load-levelling) applications. It differs from the sodium-sulfur concept in that the cathode material is comprised of a sodium chloraluminate electrolyte containing a dispersed current collector, and the cathodic reactant is a metal chloride such as antimony trichloride[43]. With this choice of materials, and a sodium anode material and beta-alumina solid electrolyte, the battery is able to operate at a lower temperature of about 200 C. This lower operating temperature should promote longer life for the electrolyte (which also serves as a separator as in the sodium-bromine battery) and reduce the rate of corrosion attack on cell components. An added benefit is that at this temperature, silicone rubber can be used for seals in contact with sodium instead of the glasses needed in the sodium-sulfur battery. Glass tubes have been used in the laboratory to contain the cathode mixture, as Table 2 shows, while glass-to-metal seals may be necessary in contact with the cathode mixture in the cell designs incorporating tubular electrolytes.

Life tests performed both with the early cell design (disc electrolytes) and the later design (tubular electrolytes) showed that ceramic failure was primarily by sodium penetration with the former, and by cracking with the latter which lead to internal shorting[43].

Potassium - Sulfur Batteries

The Dow Chemical Company investigated this analog of their sodium-sulfur battery system[44] under contract to the NASA. Instead of sodium-ion conducting, hollow glass fibers, their potassium-ion conducting counterparts were used in the type of configuration shown in Figure 5. A totally satisfactory ceramic materials for the tube sheet was not found, also, as with the sodium-sulfur batteries, the life was limited by the physical failure of the glass fibers at the junctions between the fibers and the tube sheet.

Lithium - Metal Sulfide Batteries

This battery system does not use a solid ceramic electrolyte. Instead, solid lithium alloys (anodes) and metal sulfides (cathodes) are used with a molten eutectic mixture of alkali metal halides as the electrolyte. The battery operates at about 400 C, and as might be expected corrosion problems are severe, and the requirements for the separator materials pose a materials problem. At the operating temperature only inorganic or ceramic materials are suitable candidates to physically separate the anode and cathode reactants, and to provide an ionic but not electronic conduction path. Reference (45) summarizes the use of ceramics in lithium-metal sulfide batteries.

Argonne National Laboratory[45], Rockwell International Corporation, Atomic International Division[46], General Motors Corporation[37], Eagle-Picher Industries, Gould Incorporated and the Catalyst Research Corporation are all involved in the development of this battery system in the U.S., with funding being supplied by corporate management, EPRI and ERDA. The materials of construction are basically similar for each type of cell developed by the various manufacturers, and specific details are beyond the scope of this report. To give some idea of the cell designs being considered and under development, and the ceramic materials used, Figure 7 shows an 150 watt-hour cell built by Atomics International Division, for Argonne, and Figure 8 another engineering cell built for Argonne National Laboratory with a capacity of about 100 ampere hours.

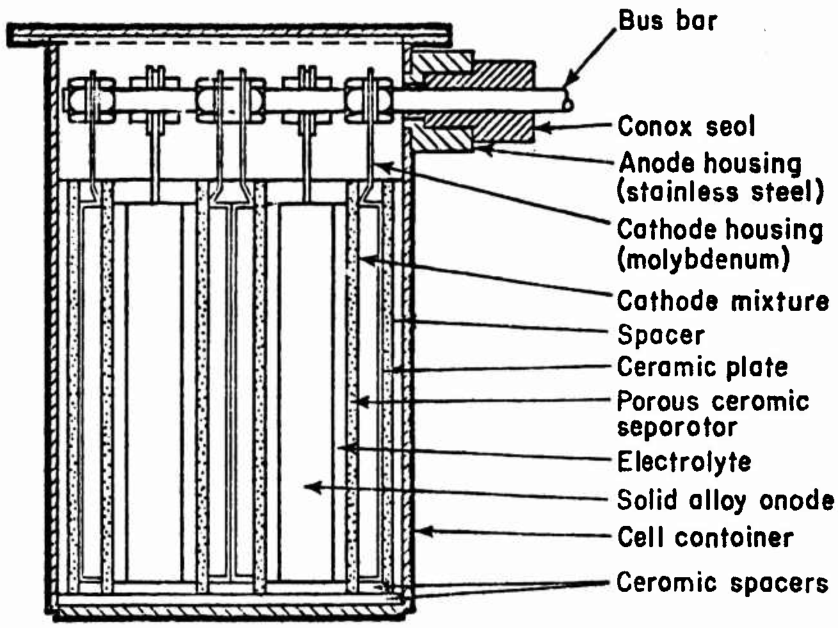

FIGURE 7. SECTIONAL VIEW OF AN 150 WATT HOUR LITHIUM-METAL SULFIDE CELL BUILT BY ATOMICS INTERNATIONAL.

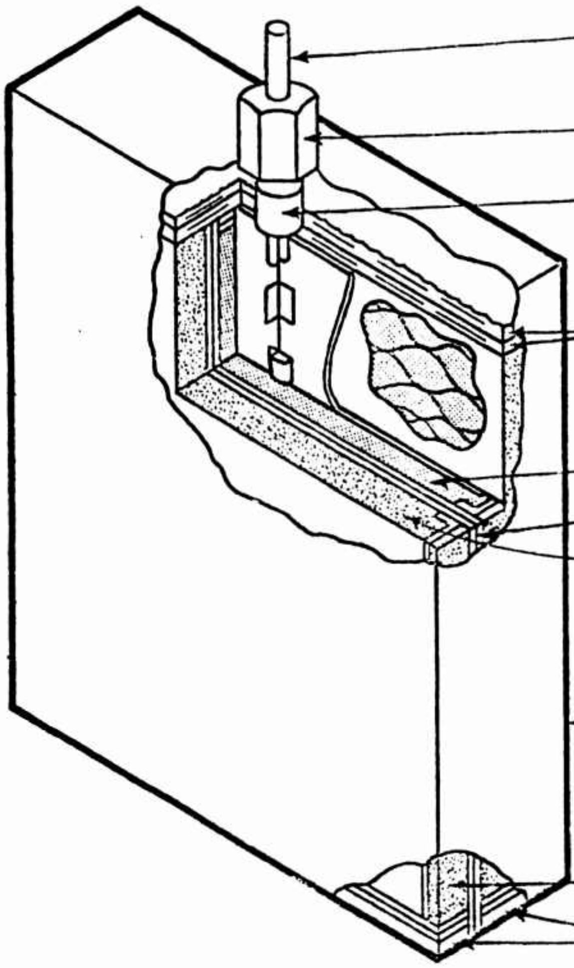

FIGURE 8. CUTAWAY DIAGRAM OF A PROTOTYPE 100 AMPERE HOUR LITHIUM-METAL SULFIDE CELL EVALUATED AT ARGONNE NATIONAL LABORATORY

Referring to Table 2, ceramic materials are primarily used as separators and spacers, as coatings and in terminal feedthroughs. Boron nitride cloth has been shown to be effective as a separator and is used in conjunction with a zirconia cloth acting as a particle retainer[45,46]. Particles of active materials must be prevented from moving from one electrode compartment to the another to prevent cell shorting. Unfortunately, boron nitride cloth is too expensive for commercial hardware, and alternative materials are being sought. Flexible separators being evaluated include boron nitride felt or paper, a mixture of this nitride with yttria and asbestos, an yttria felt, and zirconia cloth. Rigid materials under investigation include aluminum nitride felts[47], silicon nitride[46], rigid yttria and powdered magnesia[48].

For the feedthroughs, several approaches have been proposed, including a compression type, a brazed ceramic type and a "ram" seal. The compression type is a mechanical feedthrough which incorporates a compacted boron nitride powder seal, an alpha-alumina upper insulator and a beryllium oxide lower insulator[45], as shown in Figure 9(a). The brazed ceramic type such as in Figure 9(b) is similar to the ceramic-to-metal seals used in nickel-cadimium batteries, and described earlier, except metal or ceramic brazes have had to be developed to withstand the more corrosive environment within the cell. In the ram-type feedthrough, being developed by Ceramaseal, the metal feedthrough housing is forced around a rigid ceramic insulator. Further details are not available at the present time.

For certain type of cathode formulation (incorporating FeS_2) attack on the cathode current collector is severe, and conductive coatings have been considered to prolong the service life. Boron nitride, titanium nitride and ironboride, for example, have been investigated[45], and the results show that the coatings can function satisfactorily if there are no flaws which extend down to the substrate metal, thus permitting corrosion to occur. Spalling is another problem that has been identified, and results because of a mismatch in thermal conductivities.

Lithium - Metal Chloride Batteries

Just as the sodium-metal chloride battery system has bound chlorine as a cathode reactant, so does the lithium-metal chloride battery system.

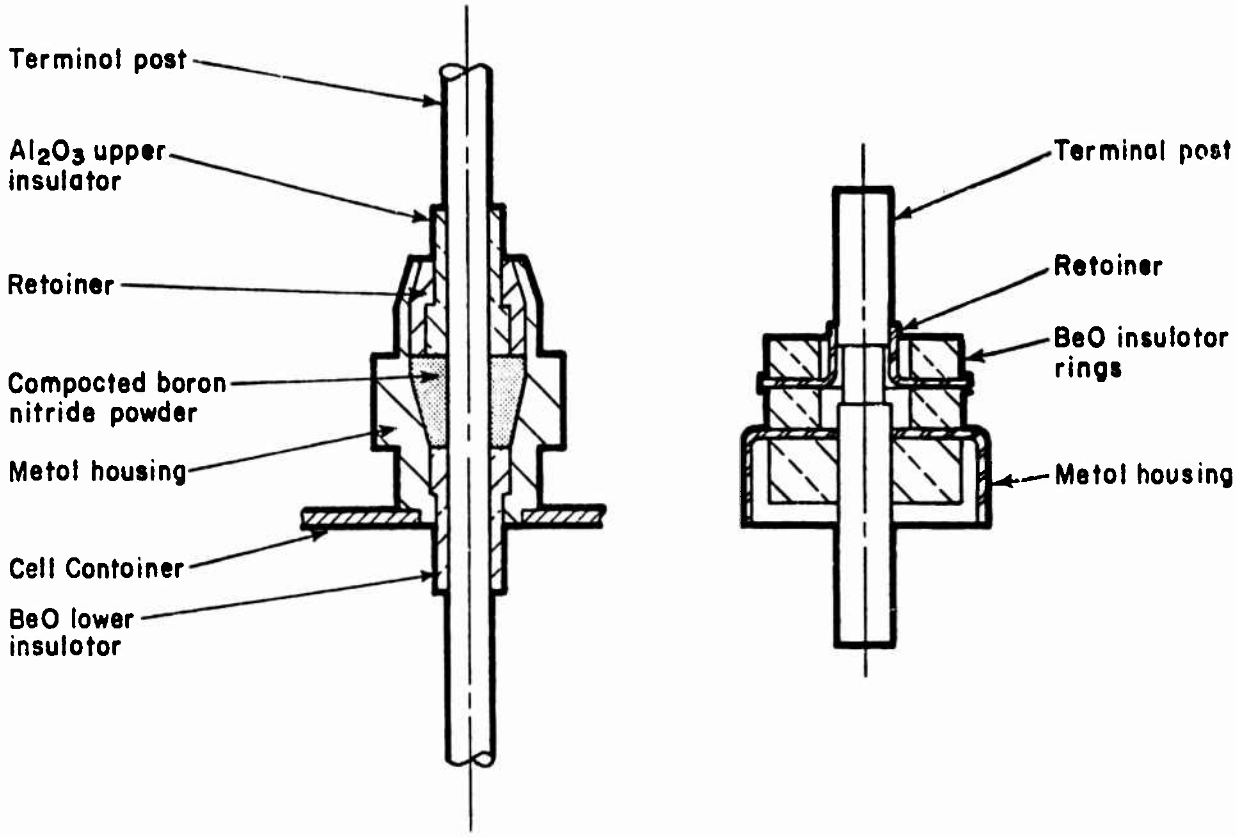

FIGURE 9. TWO TYPES OF FEEDTHROUGH BEING DEVELOPED FOR LITHIUM-METAL SULFIDE CELLS.

In this case the chloride (introduced as tellurium chloride) is immobilized on a porous carbon matrix. As with other developments in high-temperature batteries a lithium alloy (Li-Al) is used as the anode material, while the electrolyte is comprised of a KCl-LiCl eutectic mixture melting at about 350 C. In the battery system being developed for the Army by ESB Incorporated[49], a boron nitride separator is used. The boron nitride roving is preformed into a pocket into which the cathode assembly is placed during cell fabrication. The mats (two for each preform) are sprayed with a binder solution then formed around a mandrel and allowed to dry. Earlier problems with the boron nitride preforms were uneven thickness distribution, and the poor wettability of the pure boron nitride fibers themselves. Both these defects led to uneven electrolyte distribution and hence uneven current density distribution and utilization of the active materials. The wettability problem with boron nitride is being investigated by ESB Incorporated and Argonne National Laboratory.

Various types of feedthrough are under investigation including both "hot" seals and "cold" seals. The former are subjected to the same temperatures as the operating cells. A suitable hot seal does not exist to date, however, solutions are actively being pursued. Boron nitride is one of the ceramic materials being incorporated into some of the "hot" seals being investigated[51,52].

Lithium-Vanadium Pentoxide Batteries

Lithium-vanadium pentoxide batteries exist as primary or thermal batteries. The latter type, which operate at relatively low temperatures ($\sim$200 C) for a thermal battery, is of interest here[53]. A sectional view of such a battery is shown in Figure 10. A lithium alloy pelletized anode is used in conjunction with a vanadium pentoxide pelletized cathode. The electrolyte is a mixture of sodium and potassium thiocyanates, and iron powder plus potassium perchlorate is used in the heat pellets. The heat reservoirs are fusible eutectic mixtures of bismuth and tin or zinc and tin, and used to control cell temperatures in use. Nickel discs were used as current collectors, while a glass-to-metal seal was used for the feed-throughs. Fiberfrax was used as insulation adjacent to cells in batteries, while asbestos was used elsewhere as insulation[53]. Zirconium heat paper

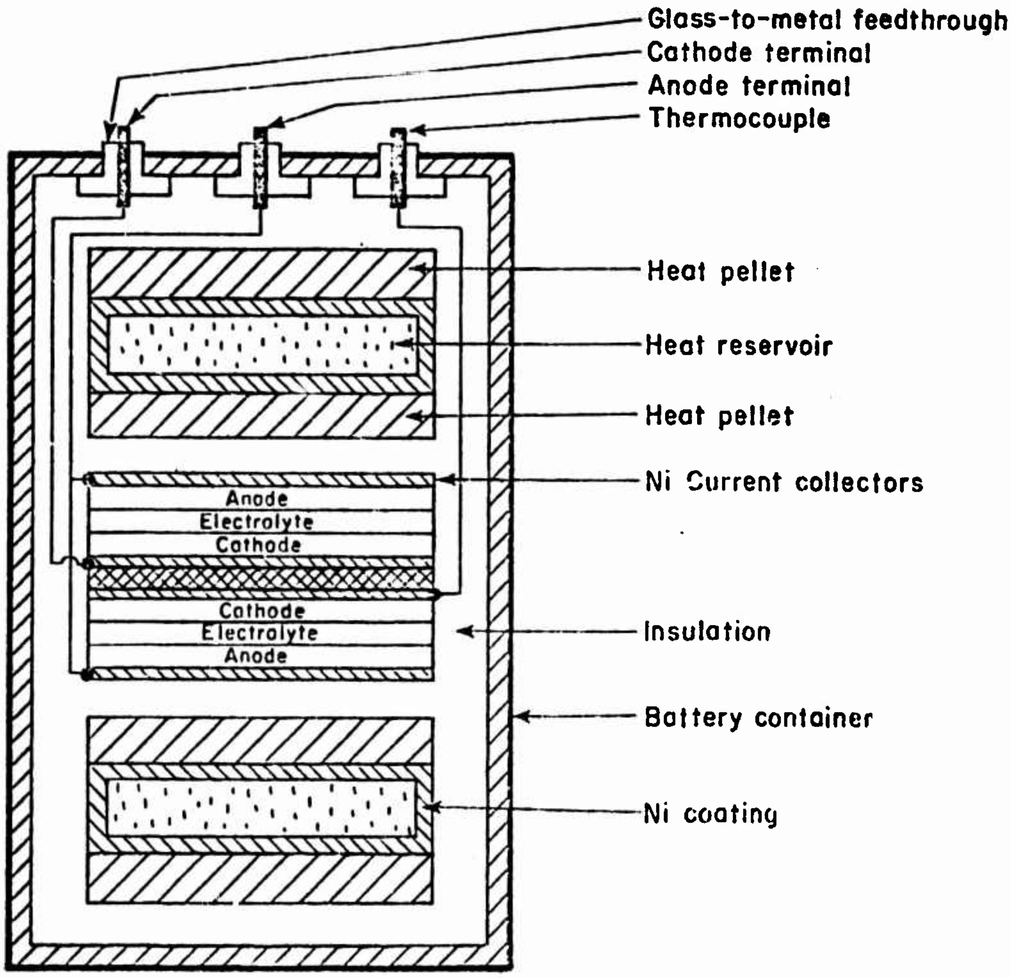

FIGURE 10. PROTOTYPE LITHIUM-VANADIUM PENTOXIDE THERMAL BATTERY SCHEMATIC.

along the side of the cells constitutes the fuse train, which is ignited by a hot wire when power is needed. Reference (54) discusses the ceramic materials used in thermal batteries.

Calcium-Metal Sulfide Batteries

These are experimental devices being developed as an outgrowth of the lithium-metal sulfide battery development program at Argonne National Laboratory[55]. Calcium is an abundant, electrochemically active, light-weight material suitable for use in high energy density batteries, and in the cells built at Argonne National Laboratory the calcium was alloyed with aluminum or silicon, paralleling the technology developed for lithium anodes. Boron nitride separators with zirconia cloth particle retainers, are the only proven satisfactory separator materials at the present time. In some cell designs a ceramic-to-metal feedthrough is used, and a seal must be formed between alpha-alumina and stainless steel[55].

Calcium-Calcium Chromate Batteries

These thermal battery systems, described in References (54), (56) and (57) differ from the calcium-metal sulfide batteries in that they cannot be recharged. They are truly primary, reserve batteries, and their construction is similar to that shown in Figure 10. In one design the electrolyte ($CaCl_2$ + LiCl + KCl) contains finely divided silica as a binder, as well as the calcium chromate as the cathode material[56]. The silica immobilizes the electrolyte when molten during operation. Eagle-Picher Industries[57] manufacture batteries which are large enough to be used for the emergency starting of tanks and other military vehicles, light aircraft, missiles and also for powering torpedos. Glass-to-metal seals for the feedthrough; asbestos and Thermoflex insulation; and glass cloth as a wrapping material for each battery section, are the ceramic materials decribed as being used in these Eagle-Picher Industries batteries.

Sodium-Sodium Batteries

To complete this survey of the use of ceramics in individual battery types a thermoelectric generator has been included which utilizes much of the technology developed for sodium-sulfur batteries. In fact this sodium-sodium battery also incorporates a solid beta-alumina electrolyte, but the system is in such an early stage of development at the Ford Motor Company, that materials compatibility and requirements have yet to be established.

Fuel Cells Operating at Low Temperatures

For the purposes of introducing the topic of fuel cells, a brief review of the concept would appear useful at this time. Fuel cells are electrochemical devices in which the chemical energy of a conventional fuel in converted directly and efficiently into low-voltage, direct-current electrical energy. A fuel cell is often described as a primary battery in which the fuel and oxidizer are stored externally to the battery and are fed to it as needed. Fuel cells consist of a container of electrolyte in which are immersed two porous electrodes, through which the reactants are brought into contact with the electrolyte. The reactants, often hydrogen and oxygen, combine to produce water and release ions and electrons. The electrons flow through an external load circuit, providing power, while the ions flow from one electrode to the other to complete the internal circuit of the cell. The electrochemical reaction is augmented by a catalyst disposed in the electrode. A fuel cell system or fuel battery is typically composed of individual cells whose open-circuit voltage approaches one volt. The cells are stacked and connected electrically in series and parallel combinations to form modules which may produce kilowatts of power at 25 to 30 volts. In addition to the energy conversion section and necessary instrumentation, a fuel-cell requires a reactant-control system and a thermal-control and water removal system.

Fuel cells can be classified as to the type of fuel used, the electrolyte and the temperature range at which they operate. Low temperature fuel cells operate up to 200 C while medium temperature fuel cells operate from 200 to 500 C. The solid electrolyte (and molten salts) high temperature fuel cells generally operate from 500 to 1000 C. Fuels are typically divided into hydrogen, gaseous hydrocarbons (methane, propane, heptane, etc.) and compromise fuels such as methanol, hydrazine, and ammonia. The classification used in this study categorizes fuel cells by the type of electrolyte that is employed. Aqueous electrolytes, both acid and alkaline, form one category and generally operate at lower temperatures and atmospheric pressures, but those such as potassium hydroxide can be found to operate in the medium temperature range at elevated pressures. The second category includes molten carbonates, most typically a mixture of lithium, sodium, and potassium carbonates in various proportions operating above 500 C. Solid electrolytes such as the doped-zirconia, doped-thoria, and doped-ceria which operate from 500 to 1000 C form a third category. A special type of electrolyte, the solid polymer electrolyte, SPE, or ion-exchange membrane favored by General Electric has been used successfully on the Gemini and Biosatellite spacecraft programs and is planned for use on the Navy's High Altitute Super Pressurized Aerostat Program.

Table 3 summarizes the data obtained during the survey on fuel cells based on classification by electrolyte. In fact, there are many more fuel cell types than shown but only those which are practically and economically viable are considered in this study. Discussions of each system including components and uses follows. The view of fuel cells as a systems concept will not be covered, so that individual cells and their operation and materials uses will be addressed. Also, any detailed discussions on fuel processing are excluded as being beyond the scope of this study.

Those fuel cells which are presently close to commercial development are in a strict sense H_2/O_2 cells. Since these cells operate at low to moderate temperature ($\leq$ 200 C) a separate step is necessary to process the hydrocarbon fuels, usually a reaction with steam known as reforming, to release the hydrogen. Separate steps are probably not necessary at higher temperatures, and the very high temperature ($\sim$ 1000 C) cells may be able to utilize the CO as well as the H_2 resulting from the reforming reaction.

Aqueous Fuel Cells

The phosphoric acid (H_3PO_4) fuel cell being developed by the Power Systems Division of United Technologies Corporation, with the backing of nine investor-owned electric utilities and a number of gas industry companies

TABLE 3. USES OF CERAMICS IN FUEL CELL SYSTEMS

System	Electrolyte	Electrodes	Matrix
(1) Aqueous	KOH, H_3PO_4, H_2SO_4, CF_3SO_3H	Ni, Pt, Carbon, WC	Asbestos, K_2TiO_3
(2) Molten Carbonate	Li, Na, K Carbonates	NiO, C, Si	Porous Al_2O_3, Powdered MgO
(3) Solid Electrolyte	Doped-Zirconia, Doped-Thoria, Doped-Ceria	Ni or Co Stabilized ZrO_2, Ni, Praesodymium Oxide, $LaNiO_3$, SnO_2-In_2O_3	---

called TARGET (Team to Advance Research for Gas Energy Transformation) and the Electric Power Research Institute[58], is probably the closest to commercial adoption. Support from the Federal Government through ERDA was directed toward improving UTC's technology of the FCG-1 in order to bring a first-generation 27-MW fuel cell power plant into commercial service by 1980[59]. The cell uses concentrated H_3PO_4 at 150-200 C as an electrolyte, with noble metal electrocatalysts (e.g., platinum), supported on graphite as electrodes, and naptha as the fuel reactant. High costs of platinum are a major problem and attempts to reduce these by decreasing noble metal particle size[60] resulted in unstable electrodes, with particle growth and loss of performance taking place. Replacement of noble metal catalysts with less costly materials has been receiving a good deal of interest. Traditional non-noble metal catalysts such as finely divided nickel or silver are not stable in the hot H_3PO_4 electrolyte. At present, only Pt-metal catalysts provide sufficiently rapid reactions. Ceramic materials (e.g., carbides and oxides) are reasonable candidates for replacing the Pt-metals.

The requirements are severe. Not only must the catalyst be a good electronic conductor, stable at high oxidizing potentials in the strong, hot acid, but catalytically active also. This last requirement is complex. When used as the fuel electrode it includes a lack of sensitivity to poisoning by carbon monoxide. For the air electrode, the catalyst must be capable of reducing O_2 to OH^- and preferably not to HO_2^-, the peroxide ion.

Several ceramic materials are finding use as electrocatalysts. Tungsten carbide has been studied for use in acid fuel cells[61]. Sodium tungsten bronzes (Na_xWO_3) have been used as oxygen catalysts but the high activity which was observed appears now to be due to platinum particles accidently introduced[62]. A similar enhancement effect was noted with Sb-doped SnO_2 with small amounts of platinum[63]. The amplified catalytic activity of the platinum surface via the ceramic oxide may lead to replacement of at least part of the noble metal in air-electrode catalysts, under sufficient control. Various transition metal perovskites have been studied as electrocatalysts for the air-electrode but they are not stable in acid solutions and are suitable only for alkaline or neutral cells. Some of these include $LaCoO_3$ doped with alkaline earth ions[64] and RuO_2 and IrO_2[65] which reduce O_2 to OH^-, leading to improved efficiency over metal catalysts.

Oxygen electrodes consisting of metal oxides with a perovskite structure and represented by the general formual (Nd,Sm) $(Ba,Ca,Sr)_x$ $CoO_{3-\delta}$ where $0.01 \leq x \leq 0.09$ and $0 \leq \delta \leq 0.5$ have been suitably used in Japan [65].

More recently, the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) has been conducting work internally and on a joint contractual basis with ERDA to develop improved electrode materials with reduced costs for use in acid fuel cells. Sulfur coated platinized platinum gauze electrodes in H_2SO_4 cells did not prevent poisoning of the electrode for the H_2 oxidation reaction and were found not to oxidize CO at a rate higher than clean platinum electrodes. The study at MERADCOM was to extend to H_3PO_4 cells and other sulfur-covered electrodes (Raney-platinum and sulfur-covered Raney-platinum on WC electrodes) but was recently discontinued. A current study is aimed at the use of tungsten carbide in pellet and powder form as electrode materials to be compared with the performance of platinum black pellet electrodes. This work has just begun.

A new class of electrically conductive, high-surface area materials as catalyst-metal supports for fuel cell electrodes has been developed by UOP Inc. and Energy Research Corporation (ERC) for phosphoric acid cells under funding by both MERADCOM and ERDA. Catalyst materials which are prepared at UOP Inc. are fabricated into electrodes by ERC. The support materials are composite structures of thin film carbonaceous polymers chemically bonded to high surface area refractory substrates (Al_2O_3 based). They are proprietary materials of UOP Inc. named Kocite impregnated with platinum to produce the electrocatalyst [67]. They are evaluated as an air and/or fuel catalyst by fabricating PTFE-bonded, gas diffusion electrodes from them (using a Kynol composite matrix fabricated by ERC) for use in H_2-O_2/air fuel cells and H_3PO_4 electrolyte. The catalysts are produced by the pyrolysis of hydrocarbons onto high-surface-area Al_2O_3 and impregnated with platinum at levels ranging from 0.5 to 10 weight percent. Electrodes are prepared by ERC using a process consisting of wet blending the electro-catalyst with a PTFE powder within a petroleum distillate solution. A Calendering operation is used to form a catalyst layer which is then pressed (2000 psi) onto either a tantalum screen or a porous graphite current collector and then sintered at 335 C in a nitrogen atmosphere [68]. Typically, the catalyst layer is 0.005 cm thick with a 5 mg/cm^2 loading of the catalyst and contains 30 weight percent PTFE. Platinum loadings range from 0.025 to 0.50 mg/cm^2. Performance of the electrodes varies with particle size of the Al_2O_3 substrate, improving with a reduced size. MERADCOM has reported in March, 1977, that the performance of Kocite^R electrodes doped with 0.5 mg Pt/cm^2 surpassed the contractual goal of 0.6 V terminal voltage at 100 ma/cm^2. The best cathodic performances were in air 0.6 V at 100 ma/cm^2 and 150 C, and 0.63 V at 100 ma/cm^2 and 180 C. Higher performances were achieved in fuel cells using SiC matrices where the air performance reached 0.66 V at 100 ma/cm^2 and 0.57 V at 200 ma/cm^2 and 180 C. Platinum sintering occurred, but high platinum surface areas were still observed after 500 hours. Alumina was leached from the Kocite^R by the phosphoric acid but this does not effect the lifetime of the electrodes. Experiments with 5 percent CO in H_2 mixtures as fuel indicate that Kocite^R anodes have a higher CO tolerance than 2 mg/cm^2 platinum black electrodes.

EPRI funded work at Case Western Reserve[69] covers transition metal catalysts (Co, Fe, Ni, etc.) deposited on graphite electrodes for acid fuel has been reported. The National Bureau of Standards has been studying the replacement of platinum with WC, MO_2C, TaC, and NbC for fuel electrodes in H_3PO_4 cells[70]. The U.S. Army has been studying degradation of carbon supported platinum catalysts via Auger electron spectroscopy to learn the nature of the chemical interactions which lead to loss of surface area and catalytic active sites through sintering and/or solution and recrystallization of the platinum particules[71]. The effects of adding stabilizing ions (Al^{+3} and Th^{+4}) to supported platinum catalyst systems and incorporating refractory metals such as W, Mo, and Rh into the structure reportedly have little effect on retardation of the sintering rate of platinum[72]. Exxon has uncovered a catalyst support system using platinum crystallites supported on activated carbon that maintain small, stable sizes after test exposures up to 750 hours, although the reasons for this stability are not clear. Normally platinum sinters rapidly when supported on carbon black or graphite.

Little emphasis has been given to sulfuric acid electrolytes as less attention seems to be directed toward its use in fuel cells. It has several disadvantages: it is highly corrosive, viscous when concentrated and has a high heat of dilution; it has considerable oxidizing power and may yield hydrogen sulphide, a serious catalyst poison on reduction. However, its use in fuel cell program contributes to materials studies and effects which have been applied to other acid systems. Studies in Canada involving agitated bed electrodes of Mo-O-S, W-O-S, Cu_2S and activated carbon electrocatalysts for oxidation of methanol fuel in an H_2SO_4 electrolyte revealed that agglomeration of particles reduces the effective catalytic area and, therefore, decreases performance[73]. A lower limit on the particle size is therefore imposed.

Organic acid electrolytes such as trifluorosulfonic acid monohydrate (TFMSA·H_2O) have received much attention recently for development of future systems. It enhances the oxidation rate of hydrocarbons relative to phosphoric acid. It also improved cathode performance and anode tolerance to CO poisoning. ERC has shown that the activation energy for oxygen reduction in TFMSA was considerably lower than in H_3PO_4. Projects supported by MERADCOM have dealth with H_2-O_2 and H_2-air fuel cells using TFMSA electrolyte at ambient temperatures, quartz and Kynol matrices, carbon supported platinum electrodes and tungsten carbide anodes. Silicon carbide matrices are also being investigated. Cell performance equivalent to phosphoric acid at 130 C was obtained with a 50/50 acid water mixture of TFMSA operating at room temperature, and with standard fuel cell components[74]. Teflon wetting which resulted in flooding of electrodes which are used with H_3PO_4 cells did not occur with the aqueous solutions. Cell potentials after 1000 hours and 100 ma/cm^2 were 0.75 V for H_2-O_2 and $\sim$0.65 V for H_2-air using 2 mg/cm^2 Pt loaded electrodes. The American University, also funded by MERADCOM, has investigated matrix materials for TFMSA cells[75]. It was reported that organic matrices degrade rapidly and pressure compensation was necessary to resolve the flooding of the electrodes due to wetting of Teflon by TFMSA. Boron nitride and a 75 percent Ta_2O_5- 25 percent PTFE composite developed by ERC are being used for matrices for electrode materials. The U.S. Army's internal program is aimed at improving both indirect and direct oxidation fuel cell performance using TFMSA electrolytes with experiments carried out on smooth platinum and platinized platinum electrodes. Oxidation rates of H_2, H_2 + 3 percent CO, and H_2 + 10 percent CO mixtures were substantially higher in TFMSA than either H_2SO_4 or H_3PO_4. The presence of carbon monoxide did not poison the platinum catalyst as severely in TFMSA as in the inorganic acids. Propane has reacted at a faster rate in the organic acid than the other two. Also, reaction rates of methane, ethane, propane, and butane were all found to be higher in TFMSA than in H_3PO_4 under similar conditions.

Although a great deal of effort has been expended by NASA to develop alkali fuel cells, their relatively low operating temperatures (20-200 C) and less corrosive attack on metal and other materials as opposed to acids, require less utilization of ceramic components. The most often used alkaline electrolytes are potassium hydroxide solutions. Use of air rather than oxygen places economic and design constraints on the KOH cells since air contains a variable but small amount of carbon dioxide which will react with hydroxide ion to give the considerably less conducting bicarbonate, therefore, requiring decarbonation techniques. An excellent summary of the alkaline fuel cells developed by NASA for the Apollo Space Program is given in Reference (76). Data from the Alsthom/Exxon alkaline fuel cell program funded in the past by EPRI have indicated a 130 mv advantage for KOH as compared to phosphoric acid at 70 C[(77)]. In addition, stable non-noble metal catalysts such as Raney nickel are known for alkaline systems but not for acids, and plastic construction materials are compatible with the KOH electrolytes. The open areas in their all-plastic frame form electrolyte chambers which are fitted with ribbed separators and anode and cathode membranes. Bipolar, carbon-filled current collectors, in their own non-conductive plastic foams, are glued directly to the central frame and electrodes using conductive adhesive in the active regions. Total cell thickness is designed to be 1.3 mm. Hydrogen manufacture is by steam reforming with decarbonization by "Catacarb" scrubbing, cyclic decarbonation and a proprietary CO_2 preremoval system.

In a NASA sponsored program, United Technologies Corporation has used a form of K_2TiO_3 called Fybex to replace asbestos as the matrix material in a KOH fuel cell for the Space Tug Program. Performance decay rates were significantly lower than cells made with asbestos matrix material (2 μV per hour as compared to 10 μV per hour). The potassium titanate is filtered onto gold/platinum catalyst electrodes prior to assembly. The cells were prone to crossover failures after about 5000 hours of life.

Fuel Cells Operating at Elevated Temperatures

Molten Carbonate Fuel Cells

The prime candidate for the second generation fuel cell for use in utility applications is a molten carbonate cell. Cells of this type operate with a molten potassium, sodium, lithium-carbonate electrolyte paste in a ceramic particle matrix (Al_2O_3, MgO, ZrO_2, etc.) at 600-700 C using nickel electrocatalysts. The major problem with these cells is a limited cell life due to sintering of the catalysts and corrosion of the construction materials. UTC has been workin on a second-generation molten carbonate cell (RP114) sponsored by EPRI but few details are given. Naphtha and Number 2 fuel oil were successfully processed by steam reforming for use in the cells. Since CO/CO_2 sensitivities are not a problem, fuel processing in general is simpler. The ERC program sponsored by ERDA utilizes a binary or possibly ternary mix of alkali metal carbonates contained in a β-lithium aluminate matrix(78). It is complex mechanical and thermodynamic entity whose role is not yet fully understood. Relative amounts of carbonate to aluminate, carbonate composition, and the effect of additives on the aluminate determine performance and life of the cell. NiO cathodes are stable and insoluble in the electrolyte. Nickel anodes sinter with time but small additions of chrome and iron seem to stabilize cell performance. The Institute of Gas Technology is engaged in a proprietary program for UTC and is funded by ERDA to: (1) determine cell performance of present generation technology using feed gases resulting from conversion of coal, heavy oils, etc. and (2) improve performance and stability of present generation technology required to satisfy commercial objectives of ∿$200/kW and a 5-year operating life. No information is available on these programs. The Stanford Research Institute approach uses a direct coal/air power generation concept. This ERDA funded study involves direct electrochemical oxidation of carbon in a molten carbonate cell. The carbon anode is derived from coal and when combined with an air cathode, allows for the direct generation of electricity(79). The cell uses a molten carbon electrolyte, with a carbon anode in an Al_2O_3 sheath, graphite counter electrode and lava heat baffles. Cell voltages between 1.0 to 1.2 volts have been observed.

Two patents describe UTC involvement in molten carbonate fuel cells. One(80) describes electrodes comprised of ceramic cloth or woven ceramic strands composed of fiber bundles coated with an electrocatalyst preferably nickel or gold. The woven cloth provides two distinct porosites. A resilient flexible ceramic fabric matrix is described(81) which is resistant to themral shock and makes electrolyte replenishment possible by wicking.

A partially stabilized Y_2O_3-ZrO_2 felt comprises the matrix while the anode is nickel felt, the cathode is copper felt, and current collectors are stainless steel. The ZrO_2 matrix is made from 0.100 inch thick fabric compressed to 0.050 inch and has 90 percent porosity. The matrix extends into a reservoir of of molten electrolyte (Li_2CO_3 32 percent; Na_2CO_3 33 percent; K_2CO_3 45 percent). Outputs of 0.6 volt at 275 mA/cm^2, and lifetimes in excess of 600 hours were obtained.

Solid Electrolyte Fuel Cells

The most studied solid oxide fuel cell system is that of Westinghouse or General Electric both of which use stabilized zirconia as a solid oxygen-ion-conducting electrolyte in cells that operate at 1000 C[82]. Catalysts are not required. The Westinghouse cell[83] (Figure 11) uses nickel as the fuel electrode and a conducting oxide, such as tin-doped indium oxide, as the air electrode. The major problems lie in fabrication of thin electrolyte layers and the lifetime of the interconnections between cells. High temperature fuel cells are very suitable as larger base-load utility power plants. Their waste heat can be used either by a bottoming cycle or by a coal gasifier of by both. Close integration, as in the Westinghouse design, can improve the energy efficiency of the coal conversion process. Low temperature fuel cells require clean fuels, however, high-temperature cells (solid electrolytes) do not have such narrow tolerances on clean fuel. Their processing requirements are, therefore, not very stringent. The increase of reaction rates due to the high temperatures helps the fuel cell approach its potential for high efficiency. Thinner solid electrolytes were used in the Westinghouse study (0.002 and 0.004 cm) than in the G.E. study (0.020 cm). The ohmic potential losses were grater for the G.E. solid electrolyte due to the thickness and this lead to lower efficiency. The G.E. study used a steam bottoming cycle, low-Btu gas and air as the oxidizer. The Westinghouse study considered three integrated cases: (1) the fuel cell and steam bottoming cycle were integrated, (2) the fuel cell and gasifier were integrated and (3) all three were integrated. The gasifier/fuel cell integration represented a version of Westinghouse's "Project Fuel Cell" study. In that concept, the fuel cell is inside the gasifier to maximize heat and mass transfer from the fuel cell.

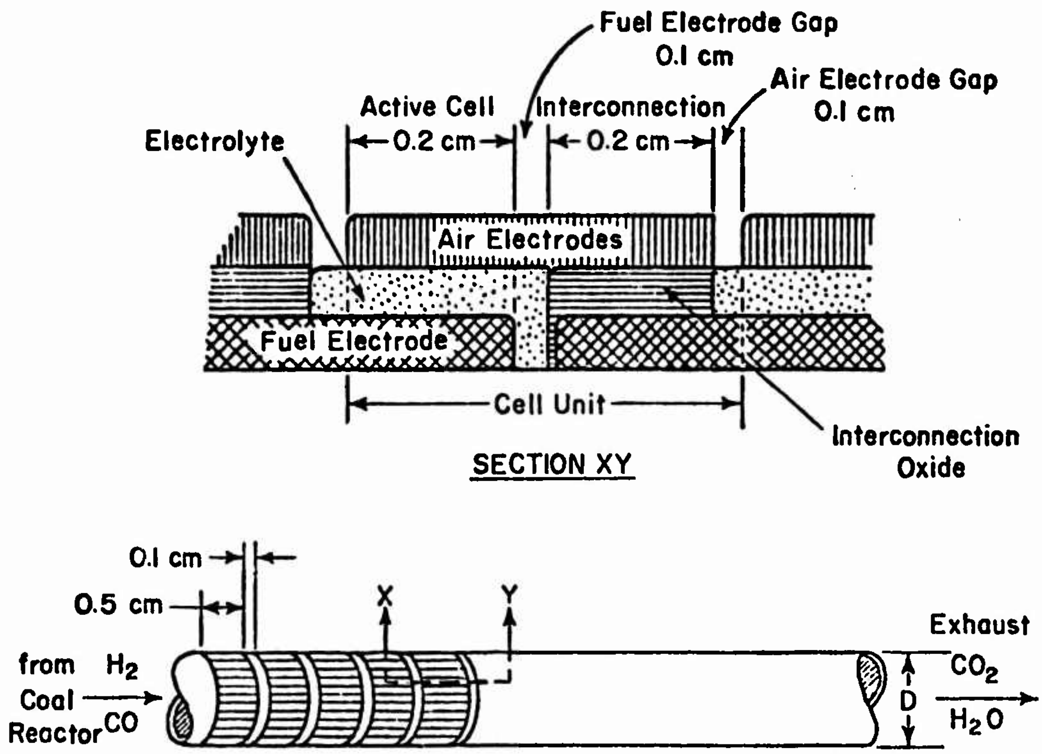

FIGURE 11. STRUCTURE OF THE WESTINGHOUSE HIGH-TEMPERATURE, SOLID ELECTROLYTE FUEL CELL.

Based on information given in Reference 82

The Westinghouse fuel cell is comprised of stacks constructed by sequential application of 20-50 μm component layers on a porous stabilized zirconia tube, which allows rapid diffusion of the fuel gases and their oxidation products. The fuel electrode is constructed of Raney nickel or cobalt dispersed through a highly porous skeleton of stabilized zirconia while the air electrode is finely divided praesodymium oxide in a skeleton of stabilized zirconia. Tin-doped indium oxide was used as the current collector. Electrolyte and interconnection layers were made by either CVD or an electrochemical vapor deposition of Y_2O_3-stabilized ZrO_2, or by reactive sintering to form CaO-stabilized ZrO_2. Interconnections to series connect adjacent cells were fabricated by CVD of chromium sesquioxide or by sintering Mg-doped cobalt chromite. Leakage of hydrogen through the interconnection, electrolyte and at the electrolyte interconnection junctions in five-cell stacks was responsible for poor performance and degradation. Improvements were made with better electrolyte and interconnection materials and fabrication techniques. After 30 hours of operation at 530 mA/cm^2 on air and H_2 + 3 percent H_2O as fuel, the voltage at that current density had fallen by 10 percent from the initial value. Hydrogen leakage caused degradation of the indium oxide component of the air electrode, therefore leading to a conductivity loss. Extensive cracking of the porous tube beneath the interconnection bonds and at the electrolyte-interconnection junctions were the cause of hydrogen penetration. This was thought to be due to stresses introduced during battery fabrication because of the difference between the thermal expansion properties of the chromium sesquioxide and the stabilized zirconia tube and electrolyte. The ECAS study demonstrated that the fuel cell subsystem in a fuel cell power plant must, for economic reasons, have a useful life in excess of 30,000 hours, three orders of magnitude greater than has been demonstrated[84].

In a current ERDA program, Westinghouse is concentrating on the interconnection problem. Candidate materials will be identified to meet the following five criteria: (1) stability in air and fuel gas; (2) resistivity in the working environment of less than 50 ohm-cm; (3) thermal expansion characteristics compatible with other fuel cell components; (4) non-reactivity towards other components, and (5) fabricability as a gas impervious layer 40 micron or less in thickness. Emphasis will also be placed on fabrication of the porous tube substrate to precise specifications.

The use of alternate electrolytes such as gadolinia-ceria solid solution (to be discussed in a later section) will be investigated. Less information is available about the General Electric design and materials of construction; however, they appear to be similar to the Westinghouse concept. Cobalt chromite is used for interconnections and indium oxide doped with tin is used for the air electrode.

A joint ERDA/NBS program involves a study of the long term property effects of Y_2O_3 and Gd_2O_3-doped ceria[85]. It was found that dopant ions in stabilized zirconia migrate along grain boundaries, creating a decrease in conductivity. The electrolyte can change, giving boundary layers of higher resistance than the bulk. Space charge effects near the electrodes which result in overvoltage are possible. A composition change at the electrode-electrolyte interface can possibly interfere with the electrode reactions.

Ceria solid electrolytes doped with yttria[86,87] and other rare earths have been shown to have higher conductivity than ZrO_2. Their conductivity is ionic only, with very little electronic conductivity and may be operable at 750 C and partial O_2 pressure of $10^{-15.5}$ atm. An interesting stabilized ziroconis fuel cell which uses conical sections is under investigation in Germany[88]. It uses a Y_2O_3-stabilized ZrO_2 electrolyte with Ni on the inside as the H_2 electrode, $LaNiO_3$ on the outside as the oxygen electrode and a glass ceramic as insulating seals between individual cells. Better seal materials such as Sr-doped $LaCrO_3$ or La, Sr, Cr-oxides were an indicated need. Sintering times for disk shaped ZrO_2 electrolytes stabilized with Y_2O_3 and YbO_3 were cut in half by the addition of 0.05-0.1 weight percent Al_2O_3 when sintered at 1600 C. The thinnest disks (0.3 mm) in this German study[89] exhibited no gas permeability, even toward helium.

Yttria-doped thoria electrolyte have found use in fuel cells, but the higher ionic conductivity of the doped zirconia electrolytes has favored there for fuel cells. Also, since thoria becomes a P-type electron conductor at oxygen pressures above 10^{-6} atm, thoria electrolytes cannot be used in high pO_2 environments such as air. Like yttria-thoria electrolytes, calcia-thoria solid solutions are predominantly electron hole conductors in the high oxygen partial pressure range and become fully ionic below 10^{-6}-10^{-10} atm, the value being dependent upon composition and temperature. An Air Force sponsored study[90] showed that ionic conductivities for CaO-ThO_2

are comparable with those for Y_2O_3-ThO_2 electrolytes and are useful in the same pO_2 ranges. Both ionic conductivity and transference number increase with CaO content up to 10 mole percent of CaO but still remain inferior to those values for Y_2O_3-ZrO_2 or CaO-ZrO_2. Studies performed in the USSR showed that preparation methods including sintering, hot pressing and plasma spraying for ZrO_2 stabilized with CaO, Y_2O_3 or Sc_2O_3 produced materials with similar values for electrical conductivity if they have the same composition[91].

Principal Applications of Ceramics

The preceding survey serves to identify the principal applications of ceramic materials in batteries and fuel cells presently under development or commercially available. Such applications are listed below, and serve as the focal point for the subsequent discussions on detailed problem areas and research needs.

Batteries

Inspection of Tables 1 and 2, and consideration of the accompanying discussions, lead to the conclusion that ceramic materials find principal application in:

(1) Separators and Spacers

(2) Solid Electrolytes

and (3) Feedthroughs.

Use in liquid electrolytes is as a gelling agent or binder, and use in electrodes is usually as an inert support or an extender, or as a corrosion-resistant coating on the current collectors. Although important to the overall battery performance, these uses are minor compared with the three uses listed above. As problems encountered with the separators, electrolytes and feedthroughs are resolved, the emphasis will shift to the minor cell components. Although relatively less effort is currently being devoted to the third application, as engineering (as opposed to laboratory cells) are developed there will be a need for hermetic seals of this type to keep out the ambient atmosphere. The atmosphere can have detrimental effects if allowed to react with cell active materials. In controlled laboratory atmospheres this is a minor problem, but with alkaline electrolytes, or high-temperature batteries incorporating reactive materials such as lithium, the problem is serious.

Currently, asbestos, fiber-glass mats (low-temperature batteries) are the principal separator materials in use. Beta-alumina, or sodium-ion conducting glasses are the principal solid electrolyte materials. Glasses, alpha-alumina, beryllia, and boron nitride powder are the principal electrically insulating materials used in feedthroughs.

Fuel Cells

Ceramic materials have been identified with nearly the same principal applications as in batteries. These include use as separators or matrices and spacers, solid electrolytes, interconnecting seals, feedthroughs and as electrocatalysts. In general, studies involving ceramics have concentrated on development of highly conductive solid electrolytes such as doped thoris, zirconia and ceria, while little consideration has been given to the fuel cell system and the structural components. There is little need for ceramic structural components for the alkali and acid fuel cells which operate at relatively low temperatures. Plastics and metals have found satisfactory applications. The more corrosive environments of molten carbonates and the high temperature envieronments found with solid oxide electrolytes require stable sealant and separator materials to be found only with ceramics and/or glasses. Potassium titanate has found acceptance as a matrix for alkaline cells using aqueous KOH as an electrolyte. It has been substituted for asbestos. Boron nitride and TaO_5-PTFE composites are used as acid fuel cell matrix materials. Tungsten carbide, lithium-doped NiO, $LaCoO_3$, IrO_2, and several perovskite-structure materials are being used as electrocatalysts. Glass-ceramics and alpha-alumina are used mainly as seals and feedthroughs.

Problem Areas and Research Needs

Consistent with the approach taken for performing the survey in Task I, the identification of problem areas and research needs was considered separately for batteries and fuel cells. Although the basic technology is similar, the requirements vary, and the ceramic materials used are sufficiently different to warrant this approach.

Batteries

Separators will be discussed first, followed by solid electrolytes, and finally feedthroughs. Low-temperature battery systems usually will be considered before high-temperature battery systems.

Separators. Fuel cell grade asbestos mats have been considered as alternatives to conventional Pellon 2505 non-woven nylon material for advanced nickel-cadmium batteries[92]. In terms of the oxygen gas recombination characteristics, both materials behave similarly. However, higher end-of-charge voltages were observed with cells incorporating the asbestos material. The difference was attributed to the fact that a thinner than desired asbestos separator was used, because commercially available material was not thick enough for these evaluations[24]. A Teflon film on the asbestos separator gave more encouraging results. Further test data are needed before a decision can be made about the suitability of asbestos for this application.

Achievement of the high energy density goals for high-temperature lithium-metal sulfide and lithium-metal chloride batteries necessitates that the separator is as thin as possible and in close contact with the anode and cathode. The interelectrode distance is thus minimized. With this arrangement materials compatibility is of prime importance, and the separator must withstand the elevated operating temperature, attack by the compounds formed during discharge, the cathode materials, the electrolyte, and the highly aggressive conditions at the lithium alloy anodes. Boron nitride cloth has been shown to be a suitable material in general, but under certain circumstances problems can be encountered even with this material. In one series of tests it was found that lithium-metal sulfide cells could not be recharged because lithium was penetrating the separator and shorting the cells. This penetration was related to the purity of the nitride materials, both boron and silicon nitride. The problem could be overcome by placing an oxide ceramic cloth adjacent to the iron sulfide cathode and next to the rigid, porous Si_3N_4 material as separator. In the Argonne National Laboratory cells zirconia cloth is used to prevent the shorting, and this is referred to as a particle retainer. Atomics International Division found that giving a proprietary "oxide ceramic treatment" to the silicon nitride accomplished the same results as the oxide ceramic cloth[46]. However, cycling tests with cells containing this treated silicon nitride showed only limited life. Upon disassembly of the cell the separator was found to be severly corroded, silica particles were present in the electrolyte, and a conductive film was found on the separator, even though thermodynamically Si_3N_4 is stable at these temperatures in the presence of lithium. With a better quality silicon nitride separator material, the lifetime should be improved. Nevertheless, an oxide-treated BN cloth is bing used in the next generation cells[46].

Table 4 lists the manufacturers of these nitride ceramic separator materials. It should be noted that silicon nitride is a heavier material than boron nitride and leads to greater polarization losses in the cell during discharge with lithium-silicon alloy anodes. However, with the same anode material composition the use of boron nitride is said to result in a lower ampere hour capacity being delivered.

Boron nitride cloth is prepared from fibers by conventional fabric processing methods[45]. The nitride fibers are made by the chemical conversion of B_2O_3 precursors. Unfortunately the weave obtainable to date is too open and there is the problem of active material migration leading to capacity loss, or at the extreme in cell shorting, as mentioned earlier. Also, the received commercial material contains about 4 to 6 precent B_2O_3, and this material forms a black conductive layer in contact with lithium in less than 100 hours[93]. Pretreatment at 1700 C in nitrogen removes the B_2O_3 and a more stable material results. In contact with Li-Al alloys, where the activity of lithium is reduced, a longer life is obtained than with pure lithium anodes.

Boron nitride felt or paper would reduce the chances of migration, in addition to being thinner, and much less expensive, both desirable characteristics. With a paper separator no particle retainer would be required, but at present zirconia cloth is used with the boron nitride cloth. Although thermodynamically unst' ble (Table 5) ZrO_2 cloth is commercially available, and serves for the evaluation of laboratory cells. Yttria cloth, made by the same process as the ZrO_2 cloth, has been used successfully in place of ZrO_2 cloth[45], however, it is very fragile (the fibers are hollow) and during cell assembly must be handled very carefully.

Table 4. Manufacturers of Some Ceramic Materials Used in High-Temperature Batteries

Ceramic Material	Manufacturer/Developer
Aluminum Nitride, rigid, porous	Atomics International Division
Asbestos, fibers	Johns-Manville
Beryllium Oxide, solid	National Beryllia
	3M Technical Ceramics Products Division
Boron Nitride, cloth, felt	Carborundum Company
Boron Nitride, paper	Fiber Materials Company
Ceramic Papers, composites	University of Florida
Silicon Nitride, rigid, porous	Atomics International Division
	Fiber Materials Company
Yttrium Oxide, rigid, porous	Argonne National Laboratory
	Atomics International Division
Yttrium Oxide, Solid	Ceradyne Incorporated
	Coors Porcelain
Yttrium oxide, cloth, felt	Union Carbide Corporation;
	Zircar Products, Inc.
Zirocnium Oxide, cloth	Union Carbide Corporation

TABLE 5. RESULTS OF COMPATIBILITY TESTS WITH CERAMIC SEPARATOR MATERIALS IN CONTACT WITH LITHIUM AT 450 C

Material	Results[a]
Y_2O_3 fabric, as-received	Slight discoloration; nonconductive; some break-up of fibers in 200-1300 hr.
ZrO_2 fabric, as-received	Severe discoloration (black); conductive; mechanical failure in <500 hr.
SiO_2 fabric, as-received	Destroyed in <500 hr.
BN fabric, as-received	Discoloration; conductive;and substantial deterioration of fibers in 200-1300 hr.
BN fabric, pretreated at 1700 C in nitrogen	Slight discoloration; nonconductive; minor deterioration of fibers in 200-1300 hr.

(a) Data taken from Reference (93).

Paper separator materials are under development. One type consists of BN fibers bonded with boron nitride, another consists of BN fibers bonded with asbestos fibers. Asbestos-bonded Y_2O_3 papers also look promising in preliminary tests. References (48) and (95) describe the status of these studies. The fibers used were BN, Y_2O_3, $LiAlO_2$ and chrysotile asbestos ($Mg_3SiO_5(OH)_4$); the fibers used as binders/fillers were BN, Y_2O_3, $LiAlO_2$ and MgO. The binders and fillers serve to improve the fabricability as well as the physical properties of the ceramic papers studied. Stability tests and in-cell operation are needed before the potential for there materials can be gaged.

Wettability of separator material by molten-salt electrolytes is a problem area addressed in Reference (94). In order for a high-temperature battery to function properly, and permit the transport of lithium ions through the separator, the separator (and particle retainer if used) must be wetted by the electrolyte. Zirconia surfaces were found to be the most wettable, and carbon and boron nitride surfaces less so, thus carbon and boron nitride fabrics were difficult to penetrate. Fortunately, methods can be devized for ensuring penetration for all the materials investigated to date.

Other types of separator structure have been investigated including rigid, porous and foamed materials; coated metallic structures; and powdered materials. The rigid, porous separator materials can be prepared quite easily by conventional ceramic processing techniques such as pressing or extrusion, and the desired priority is attained by controlling compaction, particle size, sintering time and temperature; and the type and amount of volatile pore formers if used. Separators made this way are inexpensive, easy to handle, and could be mass produced. In contrast there are practical limits to porosity, weight, thickness hence strength, and failure often occurs by cracking. Also there is still some controversy over what constitutes the optimal separator structure[45]. An open metal structure (e.g. mesh, foam, expanded metal) coated with a thin layer of ceramic separator material has also been investigated. Laboratory tests with these hybrid structures were difficult to interpret because gross spalling of the coating occurred. Little information has been made available about the development work on loose powder and foamed ceramic materials. Reference[95] describes the process for fabricating foamed yttria materials, which is of interest because of its chemical stability, high porosity/low weight, the low cost of fabrication and the potential for large scale production. Problem areas being addressed are the control of pore size and size distribution, and the optimization of the organic additives. The development work on powdered ceramic materials for separators in lithium-metal sulfide batteries appears to be paralleling efforts in the U.K.[96]. At the present time yttria and magnesia powders are under investigation[97]. Other ceramic oxide and nitride powders will be evaluated in the future. MgO can meet the cost goals for the separator in lithium-metal sulfide batteries, if suitability for this application can be proven. The void fraction should be about 40 to 60 precent, and the principal particle size should be in the range of 150 to 250 microns. If hot pressed for green strength then about 15 percent by weight of (solid) electrolyte mixture can be added. Tests with horizontally configured cells have been encouraging, however, with the preferred vertical, prismatic configuration there is more concern about whether the loose powder will pack down if the cell (active materials) changes dimension during charge-discharge cycling.

Solid Electrolytes. The beta-alumina family of solid electrolytes will be discussed first followed by the sodium-ion conducting family of glasses. The latter is used in just one single battery type, whereas the former is used in several types of low- and high-temperature batteries. The general problem area for both types of solid electrolyte is that each cell depends on the mechanical and electrical integrity of the ceramic materials to separate the active materials. In practice, cycle life is limited by the cracking of these solid electrolytes (leading to shorting), the gradual increase in electrical resistivity often observed, and the loss in charging capacity.

Beta-alumina is the name given to ceramic materials having the approximate composition $Na_2O.11Al_2O_3$, but which in practice contain an excess of sodium. It has a layered structure as shown schematically in Figure 12, and ionic conductivity is achieved by the preferential transport of sodium ions through the relatively open structure between the spinel block. In single crystals of this material the electrical properties are thus highly anisotropic. In polycrystalline materials of interest in practical cell designs, the anisotropy is masked, but a trade off in resistivity is incurred. Also related to the anisotropic structure is the directional nature of

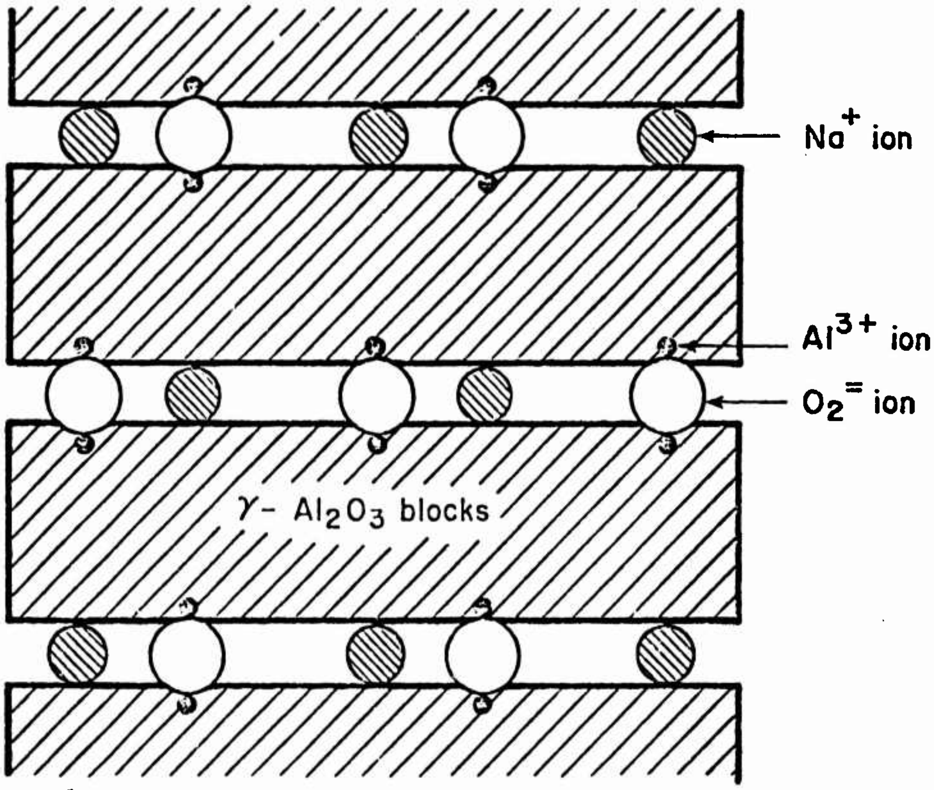

FIGURE 12. SCHEMATIC REPRESENTATION OF THE BLOCK STRUCTURE OF BETA ALUMINA

expansion and contraction during heating and cooling, as the cell is brought up to operating temperature for example. Modifications to the beta (β) structure can reduce the anisotropy, and the "beta double prime (β"), the so-called "three block" material has also been developed for use in sodium-sulfur batteries. The approximate composition of this modification is $Na_2O.5Al_2O_3$, and the conduction of Na^+ is between 2 and 5 times faster than in β-Al_2O_3 at the operating temperature of 300 C. The General Electric Company uses β-Al_2O_3, whereas Ford Motor Company uses β"-Al_2O_3 in the construction of their cells.

The sodium used in sodium-sulfur batteries must be extremely pure otherwise a certain amount of cation exchange with the beta-alumina lattice sodium atoms can occur. This exchange causes a change in lattice parameters (the spinel blocks are forced apart) and eventually can lead to cracking of the electrolyte. Experimental data show[98] that all other cations (with the possible exception of the Ag^+) cause an increase in the lattice C parameter and the electrical resistivity. It has been shown that electrolyte failure in some cells is due to K^+ exchange with Na^+ in the β-Al_2O_3 lattice structure. The potassium ion concentration must be below 1100 ppm for long life cell operation[16]. Not only must the sodium anode material not contain any detrimental cation impurities, but such cations must not be leached out of other cell components.

It is helpful to delineate the requirements for beta-alumina separator materials to appreciate the obstacles to be overcome. Cost must be low in order to keep cell costs down (cost of active material is neglible for sodium-sulfur batteries). Separator cost, however, cannot be obtained at the expense of mechanical and chemical properties, which indirectly affect all costs-for example a high resistivity means more cells are needed to obtain a desired output voltage. The ionic resistivity must be $\leq$ 5 ohm-cm at 300 C for practical cells. The density must be at least 98 percent of theoretical to prevent mechanical mixing of anode and cathode reactants. Fracture strengths in excess of 136 to 170 MN/m^2 (20 to 25 kpsi) are required for ease of handling and long life, and the material must have good resistance to thermal shock and creep. Stability in corrosive environments, possibly in the presence of residual stresses, is a necessity, and the mechanism of ceramic material degradation and failure must be understood. The material must be wetted by both sodium and sodium polysulfide to maintain a low cell internal resistance. Finally, in terms of fabrication, dimensional tolerances of less than 1 mm are needed for thickness and for tubes a perfect circular cross-section is needed to ensure uniform current density distribution. The tubes must be straight to maintain design clearances in batteries and during cell assembly the material must be stable in the chosen environment. Of course, the fabrication method must be adaptable to large scale manufacture.

Table 6 summarized reported fabrication methods, and as Reference (37) indicates, certain combinations of steps have been more popular than others. For example, Ford Motor Company and British Rail has used the combination IA1 for preparing $\beta''-Al_2O_3$, combination VC2 has been used by General Electric Company and Compagnie Générale d'Electricité for $\beta-Al_2O_3$: while Ford Motor Company, and Chloride Silent Power has looked at combination IA3 for $\beta-Al_2O_3$.

In the powder preparation step it is imperative to have uniformly mixed reactants with the desired grain structure. If the powder is to be isostatically pressed to form the green body, it must flow easily and be capable of filling the pressing bags to the required packing density in a short time period. Ford Motor Company is looking at step IV, spray drying, to obtain powders with these desirable properties. At the University of Utah[(41)] the "zeta" process has been developed to produce satisfactory powders. This process uses alpha-alumina, sodium carbonate and zeta-lithium aluminate as the starting materials, and the resulting powders has a desirable distribution of Li_2O, which means only short sintering times are required.

Both "dry bag" and "wet bag" techniques have been looked into for isostatic processing. The latter is more labor intensive, but the throughput can be higher. Both are batch processes, therefore production capacity will be limited in part by the capital for plant. Closed-end tubes can be made up to about 30 cm long provided the wall-thickness is greater than about 1mm (sintered), or up to 50 cm long if the wall thickness is greater than about 2mm (sintered). Maintaining tolerances and uniformity of the green body are problem areas in isostatic pressing, as well as the other methods of green body formation. Although good homogeneity is obtained with the electropheretic method, thickness is limited by the resistivity of the deposited ceramic frit, and the method is suitable only for thin-walled tubes. The deposition step

TABLE 6. REPORTED FABRICATION METHODS FOR THE PREPARATION OF BETA-ALUMINA SOLID ELECTROLYTE MATERIALS

Fabrication Steps		Fabrication Method[a]
Powder Preparation	I	Direct mixing of compounds
	II	Decomposition of salt(s)
	III	Gel
	IV	Spray drying
	V	Complete reaction to β- or β''-Al_2O_3
Green Body Formation	A	Isostatic pressing
	B	Extrusion
	C	Electrophoretic deposition
Sintering Method	1	Encapsulated (in Pt or inert material)
	2	Enclosed with powder (high-temperature sintering)
	3	Zone pass-through

(a) Data taken from Reference (37).

only takes minutes, but the main disadvantage with this method is that the tubes are dried on the mandrel which can take 8 to 20 hours[35]. For extrusion at acceptable rates for mass manufacture of electrolytes there is a need for a suitable binder system. The system must be non-aqueous to prevent attack on the powder. Continuous extrusion of tubing has the best potential for low cost components, but problems can be anticipated with having to close one end of the tube after cutting a length, and the texture (preferred orientation) developed in the tubes. The closure need not be beta-alumina, but could be alpha-alumina if a suitable seal could be developed. The effect of texture on the electrical properties of the tubing is a subject which requires investigation.

Sintering and annealing is normally carried out in the range between 1450 and 1850 C, and care must be taken to minimize Na_2O losses at these temperatures, especially from β-Al_2O_3 green bodies. The time and temperature profiles are critical to develop the required composition, homogeneity and grain size. The "duplex" structure of undersirable large (100-300) and small (<50 microns) grains is to be avoided. Sodium loss can be minimized by proper atmosphere control, encapsulation, and using low sintering temperature. In the preparation of β-Al_2O_3 electrolytes, another problem is to ensure that the rate of conversion to the β'' form progresses at a similar rate to the densification process. A high temperature (~1600 C) sinter for a short period of time followed by an anneal at a lower temperature, is one approach[35] to overcome this problem, and is amenable to commercial manufacturing processes. Similarly, a rapid sinter is possible at ~1600 C if the powder is seeded with $\beta''Al_2O_3$ (5 to 40 μm particles) to provide nuclei for more rapid conversion. A post sinter anneal is then not required, and electrolytes with a resistivity of 5 ohm-cm, an average grain size of 50 microns, and a density in excess of 98 percent can be achieved. However, acceptable performance of this seeded material in test cells has yet to be demonstrated. The sintering temperature can only be lowered if a transient liquid phase if formed to assist in the densification process. With the proper combination of process variables it may be possible to obtain a suitable electrolyte material by sintering at about 1450 C for three hours[35].

Some of the problems with soidum-ion conducting borate glasses are similar to those formed with the beta-aluminas. Homogeneity of the glass, dimensional tolerances, sealing the ends of the cut fibers, all can cause problems in cell fabrication and operation. In addition, the borate glasses have a high temperature coefficient of resistivity, so that relatively small changes in temperature of the individual hollow fibers can cause sizeable changes in current density. Higher current density areas are subject to additional heat generation, which exagerate the temperature differences. If at certain locations in the cell the temperature is such to over-discharge the cell, forming solid sodium polysulfides, the stresses generated can cause the fibers to break. The failure mode is more likely to be observed in cells near the end of discharge cycles, being subjected to deep depth of discharge.

With the Dow Chemical Company's sodium-sulfur cells, only small laboratory cells have been tested to date, containing about 1000 fibers ($\sim$0.5 ampere hours). Satisfactory cycle life has been exhibited if the sodium has been carefully purified. Large cells have been built (40 ampere hours) but have yet to be tested, and as such there are relatively little engineering data available on batteries of engineering interest. In the scale-up process, one problem area is the development of a suitable "tube sheet" which supports the many thousands of individual fibers, and for which an inexpensive sealing system (around each fiber) must be developed. A similar problem exists with the proposed General Electric Company sodium-sulfur battery where many electrolyte tubes are suspended in the cathode compartment within the battery container.

The reason why so many glass fibers are needed in the Dow Chemical Company cell is the high electrical resistivity of the borate glasses used, typically about 5×10^4 ohm-cm. Thus in order to minimize cell internal resistance the hollow fibers walls have to be very thin ($\sim$10 microns), and each hollow fiber can only contain a limited amount of sulfur. Fabrication of such fiber in continuous lengths can be accomplished, however the fibers are fragile, and cell assembly must be carefully accomplished. Thicker fibers would be desirable for easier cell fabrication, however, a way of reducing the cell internal resistance would have to be devized in order to meet the same performance goals. The thicker-walled fibers could be of larger diameter, thus the gravimetric energy density (whr/kg) and the volumetric energy density (whr/m^3) need not change considerably.

Feedthroughs. In general, few problems exist with the existing feedthroughs for low-temperature and thermal batteries. The cell internal environments are usually relatively non-aggressive so a true hermetic seal can be formed, with helium leak rates of $\leq 10^{-8} cm^3/sec$. The situation is different with the feedthroughs for high-temperature batteries, where the cell internal environments are aggressive because of the presence of lithium at elevated temperatures. Forming a mechanical seal to retain electrolyte, and other particles is not difficult, but making a reliable, long life hermetic seal is another matter. As discussed earlier, several approaches have been tried including the conventional ceramic-to-metal (braze); Conax-type mechanical (compressed powder); and ram seal (see Figure 9). An effort was made to produce a swaged type seal[99], but a compact, strong, leak-tight seal could not be produced.

Sintered or hot pressed yttria, beryllia and pretreated boron nitride (to remove B_2O_3 residues) have been shown to be compatible in contact with lithium at 400 C, and thermodynamically thoria and aluminum nitride are stable, hence are the prime candidates for feedthrough developments. Yttria, unfortunately is relatively expensive, and has poor thermo-mechanical properties[93]. In some tests (both static corrosion tests and in experimental cells) beryllia has been attacked by lithium, and conductive surface films formed, even though thermodynamically it should be stable[47]. In this respect, the behavior of calcium zirconate was similar. Aluminum nitride has been shown to be suitable for lithium-metal sulfide and -metal chloride batteries. However, the material is not commercially available with the desired characteristics. Research is under way both to develop low cost preparation and fabrication techniques. At the present time only cylinders and large tubes ($\sim$7cm diameter) have been prepared in the laboratory[47].

With the brazed, ceramic-to-metal seals around the positive terminal feedthrough in lithium-metal sulfide cells, the ceramic material and the braze material must withstand the operating temperature of about 400 C, thermal stresses, the chemical environment, galvanic corrosion attack, and the applied potential at the terminal during charging. For example, the braze must be sufficiently electropositive to be stable at the 2.0 volt cut-off voltage[45], and niobium appears to meet this criterion. Brazes of Nb-Ag, Nb-Cu and Nb-Au are under investigation. As an alternative approach, conventional ceramic-to-metal seals (with Mo, Mn and Ti brazes) are being considered when protected by a coating[99]. However, catastrophic attack occurs if a coating flaw is present. Ceramic braze materials are also undergoing evaluation, and will have the same constraints as the ceramic seal body. Alumina rings are being substituted for the upper two of the three beryllia rings shown in Figure 9. These are lower in cost and may be satisfactory because they are not in contact with the cell internal environment.

For the near-term, BeO, Al_2O_3 (not exposed to cell internal environment) BN and Y_2O_3 have been selected for compression-type feedthroughs. Less costly materials with better mechanical properties, higher density and less fabrication flaws, and better thermal conductivity match with the molybdenum terminal post are being sought. The substitution of BeO for the weaker BN lower insulator (Figure 9) will allow more complete tightening of the feedthrough resulting in a better seal. Solder glasses are also being evaluated as a secondary sealant on the outside surfaces of the powder[95]. Replacing the compacting nut in the conventional Conax design with a retainer plug has enable a more compact design to evolve[99]. The housing is crimped over this retainer. Cost projections for this compression feedthrough (100,000 lots) are presently about twice the cost goal of about $1.00 per unit. The boron nitride powder represents about 12.5 percent of the total cost.

Details of the Ceramoseal Inc. ram seal are proprietary, but the principle is to force an internally plated metal sleeve over a carefully designed BeO body around the terminal post[99]. The inside of the sleeve is smeared onto the ceramic surface, and the hoop stresses generated force the BeO body against the terminal. Leak rates of only 10^{-9} cm^3/sec (He) have been measured. This seal is currently being evaluated by Argonne National Laboratory, and preliminary results have not been encouraging (premature failures). Efforts are underway to reduce their size and weight.

In sodium-sulfur batteries incorporating lithia-stablilized beta alumina electrolytes, the glass α to B''-Al_2O_3 seals are attacked, discolored and pitted. Although to date failure of the feedthroughs has not been observed, the mechanism of this attack is not understood. For long life cells an understanding of the responsible parameters will be necessary so that they might be controlled. Mechanical seals, including a disc-spring type, are bing developed in the U.K. by the British Railways Board[100]. The results of their long-term cycling tests will show whether these constitute a viable approach. Semi-automatic methods can be used to fabricate these feedthroughs, and cost is expected to be less than 5 percent of the total cell cost. (Similar to the cost goal for lithium-metal sufide cells).

Cold seals, where solidified electrolyte forms the seals, have been used on laboratory lithium-metal chloride cells, where weight and dimensions need not be optimized. For fork lift truck applications where volume is of concern, the tall cold seals will not be acceptable, and short, hot seals are necessary. So far a reliable hot seal has not been developed. Factors impeding development of a satisfactory hot seal include problems with thermal expansion mismatch with the terminals, stresses induced during thermal cycling, corrosion, and electrochemical stability under the voltages experienced by the terminal posts. Development programs are under way at ESB Incorpoated[49], but results have not yet been published.

Fuel Cells

A number of problem areas involving ceramics were cited in the discussion on fuel cells included in this study. These relate generally to the need to improve seals and interconnecting materials, which cause cell failure by corrosion, cracking, etc.; cheaper and more active electrocatalysts; and more conductive solid electrolytes which may operate at lower temperatures, and enable thicker walls to be used which would ease fabrication problems and increase lifetimes. For example, stablilized zirconia has a conductivity of the order of 6 to 13 $ohm^{-1}cm^{-1}$, depending on the stabilizing element. A thickness as small as $2x10^{-5}$ cm is necessary to provide a practical value of about 5 $ohm^{-1}cm^{-1}$ for calcia-stabilized zirconia[82]. Achieving such thin ceramic layers with high reliability on a commercial scale and at low cost will require considerable efforts. An alternative may be found by using CeO_2 doped with Gd_2O_3, or CeO_2 doped with Gd_2O_3 plus MgO. Data shown in Figure 13 indicate lower resistivity values for ceria electrolytes compared to zirconia mean that ceria can be utilized in either of two ways in fuel cells: to decrease operating temperature for a given resistivity, or to decrease resistivity (increase cell capacity) at a given operating temperature. It appears that with these materials, operation temperatures around 750 C may be feasible for high-temperature fuel cells where lifetime-limiting problems with material degradation may be less severe than at the 1000 C

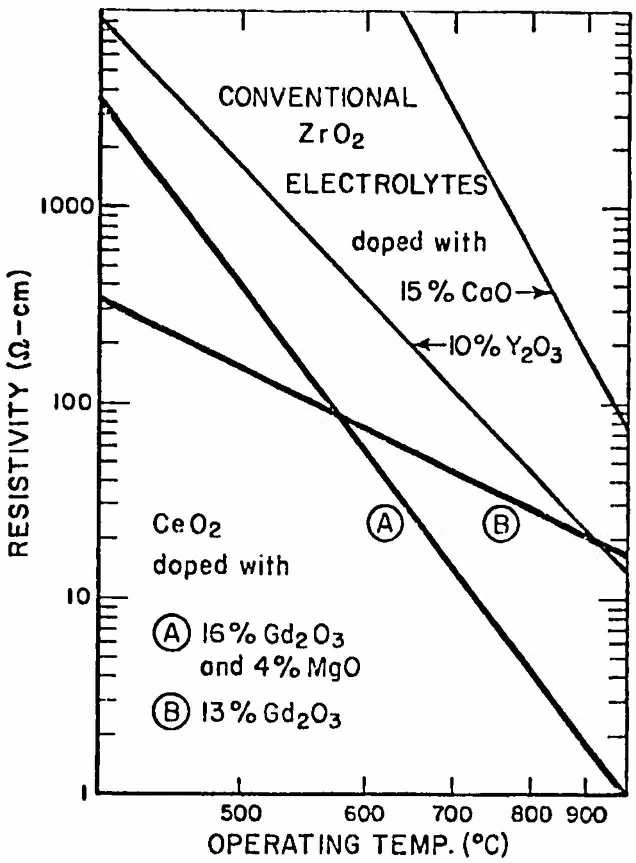

FIGURE 13. COMPARISON OF THE ELECTRICAL RESISTIVITY OF CeO_2-Gd_2O_3 SOLID ELECTROLYTES WITH CONVENTIONAL DOPED-ZIRCONIA AS A FUNCTION OF TEMPERATURE.

Data supplied by Molycorp, Incorporated

temperature necessary with ZrO_2. Besides the technical advantages of ceria, there is an economic one in that it is abundant and inexpensive. Westinghouse is currently looking at the use of these electrolytes for replacement of stabilized zirconia. The difference in thermal-expansion properties of these electrolytes will mean that new porous tube and electrode technology and interconnection materials will have to be developed.

Several other factors need to be resolved with high-temperature fuel cells. Ohmic losses need to be reduced, not only by improvement of the electrolyte conductivity, but by decreasing the contact resistance between the electrolyte, the electrode materials and the current collectors. Fabrication of cells at present is generally made more difficult by the different coefficients of expansion of the materials of construction when being cycled through the various sintering/impregnation operations. Interfaces between the gaseous fuel or oxygen, the electrolyte, and the electrode materials have not been optimized, thereby falling short of the full potential of these fuel cells. Stanford Research Institute has in part addressed some of these problems by designing a molten carbonate cell which uses molten lead as the anode and coal or coal char as a solid fuel[104]. The molten carbonate was immobilized in a porous Al_2O_3 matrix and a silver screen cathode was used. Another type of cell used a yttria-stabilized zirconia tube as the electrolyte. Both bypes of cells produced open circuit potentials well above those calculated for a lead-air cell in the temperature range 600-800 C, and for the carbonate electrolyte cell the observed voltages were within 50 mV of the values calculated for a carbon-air cell. The use of more reactive carbon increased the cell voltage as well as the CO concentration in the anode gas. An operating voltage efficiency as high as 75 percent was observed. The system offers distinct advantages in that unlike low temperature hydrogen cells, noble metal catalytic anode materials are not required and the high conductivity of the molten lead may meet a part of the low resistance cell interconnection requirements.

Battelle's Columbus Laboratories has proposed a concept similar to that of SRI in which the working voltage is generated by establishing an oxygen gradient across a stabilized zirconia electrolyte. The fuel anode consists of a molten metal oxide eutectic mixture such as PbO-Cu_2O while the air electrode (cathode) would consist of a molten metal oxide mixture with a high oxygen activity, such as PbO with 7 weight percent Al_2O_3.

Iridium screen and carbon current collectors might be used and the whole arrangement contained in an alumina or zirconia vessel. Molten metal oxide electrodes could make fuel cell assembly easier and less costly because the problems associated with sintering materials with different thermal properties would be avoided. Porous platinum, nickel-zirconia and cobalt-zirconia porous layers, and sintered cobalt chromite which have been used as anode materials in stabilized zirconia fuel cells could be replaced by a molten oxide mixture. Current densities at least as high as the solid alternatives should be sustained because of the resulting decrease in contact resistance expected. Quicker removal of the product gas (oxygen) away from the electrode electrolyte interface by natural thermal convection and diffusion processes are expected. Lower operating temperatures are projected which would reduce materials compatibility requirements favoring a longer cell life.

Not all of the problems of fuel cells are restricted to materials performance. For example, the use of asbestos as a matrix material may be subject to a Federal Government ban on asbestos products. Some materials which are needed such as yttria, nickel, platinum, etc., may not be abundant enough to proceed with large scale development of fuel cells. It has been estimated that 4.5 Kg of nickel would be required per kW of pwer and the world's total production of platinum would only satisfy one percent of the electrical power demand[105].

Attention must be directed at the development of seals and feed-throughs for high temperature fuel cells. Glasses thus far examined suffer from corrosion and degradation problems. Separation materials are not a major problem with the solid electrolyte fuel cells but do present problems in the molten carbonate cells. Degradation of the alumina matrices in these cells, predominantly by reaction with lithium, determine both the performance level and life of the fuel cell. The use of K_2TiO_3 in aqueous KOH cells appears to be satisfactory and is finding wide application. Series connector materials present a severe problem in the high temperature fuel cells based on stabilized zirconia. The connector material must be a good electronic conductor at about 1000 C over a range of oxygen partial pressures, must not react with the other components of the cell with which it is in contact and must not vaporize appreciably over the 5 year design life of the cell. Cobalt chromite appeared to be promising in the

Westinghouse fuel cell[83], but this material remains one of the weakest parts in the cell lifetime. These problems may be avoided by going to lower operating temperatures provided by ceria electrolytes but new technology and materials development will most likely be required.

The operational efficiency of fuel cells is highly dependent upon the rate of reaction at the electrodes and catalysts are needed for all but the high temperature fuel cells, including the solid electrolytes and molten carbonates. A major problem in acid fuel cells is in developing a satisfactory catalyst for the air electrode, which is low in cost and has a long life. Platinum metal catalysts are presently the only means of providing sufficiently rapid reactions. Using finer particles to bring costs down results in other problems such as sintering and agglomeration which reduce cell performance. They are not stable in hot phosphoric acid during fuel cell operation to provide the necessary lifetimes. Tungsten oxide has been finding wider use and acceptability in acid fuel cells and lithium-doped NiO is used as an oxygen catalyst in alkaline cells. Agglomeration effects also limit ceramic powdered catalysts. Research needs in the area of cheaper more reactive electrocatalytic materials, especially the cheaper ceramic oxides and carbides, is evident.

Low-temperature proton-conducting solid electrolytes which would allow construction of simple and rugged H_2/O_2 fuel cells should be developed. Presently, the leading candidates are polymer ion exchange membranes which can be made to exchange cations such as H^+ or anions such as OH^-.

There are certain chemical problems connected with membrane behavior some of which are not yet solved. For example, the ionized groups on the polymer may be hydrolyzed off in certain circumstances, and the transport of water through or along the membrane depends on a combination of physical and chemical effects. Solid ceramic proton-conductors offer more attractive mechanical properties than the polymer membranes. Active interest in England has been given to proton conductivity in phosphates based on the KH_2PO_4 structure where substitution of Na, Rb, and Cs for K ion is used to alter migration potentials[106].

Future Developments

The present comprehensive survey has been made based on past and present technology, as called for in the work statement. However, it should be pointed out that changes in raw materials availability and price; the strategic stockpiling of materials; changes in requirements; new technologies competing for the same materials; invention of new battery systems; changes in corporate R and D policies; and changes in federal R and D funding, are among those factors which could affect the R and D needs for battery and fuel cell materials, as outlined in the next section.

The anticipated impetus provided by the Electric and Hybrid Vehicle Research, Development and Demonstration Act to the sale and use of electric vehicles will provide an incentive to develop high-performance batteries, and put them into mass production. This incentive in turn could result in more R and D funds being made available, both in the private and the government sector. More opportunity will then exist for the development of such systems as advanced lead-acid, nickel-zinc, sodium-sulfur, lithium-metal sulfide and lithium-metal chloride[101].

Emphasis placed upon large scale energy conservation, the generation of unconventional fuels, and the harnessing of alternate energy sources in the future will mean that appropriate energy storage technology will have to be developed concurrently. Storage (secondary) batteries are in contention for peak-shaving and load levelling applications[102]. The batteries in contention for this application include the sodium-sulfur and lithium-metal sulfide systems; both of which employ ceramic materials for their satisfactory operations. If battery bulk energy storage is adopted in the mid to later 1980's, the installed capacity could be so large that availability of materials (1 to 5 percent of total installed electrical capacity) and production capacity could be a prime concern.

If substitute fuels, such as methanol, synthetic natural gas or hydrogen, become available in large quantities, "reformer" type, low temperature fuel cells may find consumer application. With dispersed siting, that is locating the fuel cell near the loads, transmission and distribution credits are possible, and fuel cell electricity generators become more attractive economically. Installation of a large generating capacity will mean a greater demand for asbestos products, or substitutes such as potassium titanate.

With the high-temperature battery systems there is the temptation to move in the direction of higher operating temperatures because of greater utilization of active materials, increased efficiency and higher operating current densities[102]. However, materials stability will be affected and corrosion will be more severe. There will be a greater need to develop corrosion resistant ceramic coatings if this trend is followed.

It is difficult to predict volume requirements for ceramic materials at the present time for several reasons. Many of the battery and fuel cell systems are still under development and designs have not been finalized. Also materials selection is far from complete for such systems. Unfortunately there is often an interdepence between design and materials selection because as cell design is changed, or operating conditions are altered, the materials requirements will be different. Usually the requirements are more severe, for example. However, under certain circumstances the changes can be beneficial, for example placing high-temperature batteries inside a sealed container means that individual cells need not have hermetically sealed feedthroughs. A more compact, simpler feedthrough can be designed to just physically retain internal cell materials. Another example is the so-called "inside-out" or "sulfur-core" sodium-sulfur cell. In such a cell design the highly corrosive polysulfides are contained within the beta-alumina tubes, and the sodium anode material is in contact with the cell container. The sodium is not as aggressive as the polysulfide cathode mixture and corrosion attack is lessened, therefore a cheaper container material can be used, and there is no need for a corrosion-resistant ceramic coating for the container inside surfaces. Finally, a new technology may be invented, such as lithium-ion conducting analog of beta-alumina. If such material were developed, the immediate potential applications would be numerous, and another area of R and D needs would be established.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Ceramic materials play an important role in many types of battery systems including low-temperature aqueous and non-aqueous primary, secondary and reserve batteries; and high-temperature secondary and thermal batteries. The major applications are as separator and spacer materials, solid electrolytes and in hermetic feedthroughs, but other important uses are as seals, structural components, corrosion-resistant coatings, electrolyte additives and electrode support materials. At the present time emphasis is on meeting technical objectives for the battery systems under development. Until materials compatibility, performance, life and other physical, mechanical, chemical and electrochemical contraints can be met the cost objectives cannot be met. That is not to say that the projected cost of each new development to meet the technical objectives does not play a role in the selection process for the alternatives to be pursued.

There has been expressed concern over the fact that although the demand for thermal batteries will increase, there has not been an increase in manufacturing capacity for the materials required. The inconsistent quality of the existing supplies also leaves much to be desired. The DOD/ERDA task group formed to address this problem area considered the following materials: zirconium powder; iron powder; barium chromate; calcium chromate; tungstic oxide; mica and asbestos. They concluded that the zirconium powder and chromates were the most critical materials. If the production and use of asbestos is classified as a health hazard by federal edict then an alternate insulating material must be found.

In fuel cells, ceramic materials also play an important role as separators or matrices in low-temperature devices, as solid electrolytes in high-temperature devices; and as electrode support materials in both. Additional applications are as seals, structural materials, and many of the applications, and the ceramic materials used, are similar to those used in battery systems. Also high-temperature water electrolysis technology is similar in many respects to high-temperature fuel cell technology, and some low-temperature electrolyzers resemble low-temperature, aqueous electrolyte fuel cells. The number of companies, agencies and other establishments involved in fuel cell R and D is relatively small at the present time, and less than the number of establishments involved in battery R and D. Emphasis is currently on aqueous (phosphoric acid) and molten carbonate fuel cell systems.

Specific problem areas and research needs have been identified for batteries, as listed below:

(A) Woven BN and AlN cloth are suitable separator materials for laboratory cells, but are up to two orders of magnitude too expensive for commercial cells; they are too thick, and the weave is too open, such that additional particle retainers must be used; production capacity is limited at the present time. There is a need for a substitute paper separator material which has a low cost, and which is ductile. The ceramic fibers produced for such paper materials are not suitable for use without binders and/or fillers. Suitable flexible fibers, with diameters less than 1 μm, a length to-diameter ratio of about 10^4, and surfaces conducive to mechanical interlocking would permit the manufacture of thin paper separators. If mechnical interlocking cannot be achieved, then binders/fillers which are chemically more stable than asbestos must be developed. Paper separators would obviate the need for particle retainers, hence could reduce cell cost, and simplify fabrication procedures.

(B) Until paper separators materials can be developed for high-temperature cells, efforts should continue in alternatives which have the potential for low cost, semi-automatic or automatic production. Rigid, porous separators and powdered ceramic separators warrant further investigation. With the rigid, porous type of ceramic material there is a need to improve porosity, reduce weight and thickness, increase strength, and investigate ways of preventing in-service cracking. Powdered ceramic separators are still in an early stage of development and the long term dimensional stability in prototype, vertical prismatic cells should be demonstrated. Hot pressing ceramic powders such as MgO and Y_2O_3 onto the surface of the cathode during its fabrication will help to immobilize part of the powder. If the powder does pack down in use a porosity gradient will be established from top to bottom of the cell resulting in uneven current density distribution in operation. This is to be avoided.

(C) Cell design and component design at present is a dynamic situation, and changes in one component affect the requirements for other components, e.g., changing the cell size to increase capacity by using larger plates, means large terminals are needed which in turn affects the design of the cell closure and the feedthroughs. Whereas, a ceramic material may function satisfactorily in one size and design of component, inferior performance may be obtained in other sizes and designs. There is thus the need to establish as early as possible a standard size (or group of sizes) of cells and batteries.

(D) An inexpensive method of manufacturing beta-alumina for sodium-sulfur battery electrolytes and other similar systems is needed. Cost has to be reduced by an order of magnitude for commercial cells. If extrusion is used then a better binder is needed, along with a method for closing off the tubes at one end, and a control over the texture developed during the process. If isostatic pressing is the method of choice again an improved powder is required, one with better rheological properties for faster and more uniform bag filling.

(E) The trend is towards using larger beta-alumina tubes (30 to 60 cm long) and with such large tubes homogeneity, high strength, low conductivity and small grain size are all desirable features which must be traded off against each other. In addition the number of rejects must be decreased from the 30 to 40 percent typical with these large tubes.

(F) For low temperature batteries, ionic conductivity is lower, therefore thinner, but mechanically strong beta-alumina electrolytes are needed. Goals are down to 150 μm, and 102,00 N/m^2. Electrophoretic deposition is one approach, but on-mandrel drying times are prohibitive. Times need to be shortened for a viable commercial process.

(G) Improved sealing glasses are needed to join alpha- and beta-alumina components. Presently used glasses are subject to corrosive attack in sodium-sulfur cells, especially if lithium is present, e.g., from a stabilizing additive to the beta-alumina.

(H) Long life cells incorporating beta-alumina electrolytes can be fabricated in the laboratory if care is taken to remove dissolved cations (especially K^+) from the anode compartment. One approach has been to use "metal-free" cells designs which is fine for laboratory investigations, but is not a practical solution for commercial cells. Corrosion in the aggressive environment inside the cells must be contended with. One approach has been to use the "inside-out" or "sulfur core" design, which also favors the use of simpler seals. Another is to use corrosion resistant coatings such as TiO_2. This material has to be doped to achieve appreciable electronic conductivity. Preliminary experiments with both container coatings and current collector coatings have been promising. Effort on this development should be continued. It may be possible to use a metal-clad coating as the container material itself.

(I) The problem with existing borate glasses developed for sodium-sulfur batteries is that the ionic (Na^+) conductivity is too low. Thus thin, hollow fibers have to be used which are fragile, and which make sealing to a tube sheet more difficult. If the conductivity of these glasses can be improved, thicker fibers/tubes can be used which would make handling easier, and reduce the number of fiber/tubes for a given capacity. The number of seals required per cell would decrease.

(J) There is still the need for a high-temperature, hermetic feedthrough. Mechanical strength combined with chemical stability, ease of fabrication and low cost are the demanding requirements. The problems are most severe with the lithium-metal sulfide and- metal chloride batteries where any material exposed to the interior cell environment has to withstand lithium at about 400 C. BN is stable but not strong enough for mechanical seals; AlN may be suitable but a method is needed to fabricate solid components from this material; BeO has the strength but has toxic properties making fabrication a more hazardous operation. Other materials such as $CaZrO_3$ need further study before their suitability can be assessed.

(K) Brazed and ram-type feedthrough designs are simpler and have fewer component parts, therefore have the potential for being produced at low cost. Also the simplicity of design will favor a smaller size feedthrough being developed. Reasons for the in-service failure of the ram type after a relatively short time should be found. For the brazed, ceramic-to-metal seals, brazing metals and alloys are needed to withstand chemical and electrochemical attack. It is unlikely that ceramic brazing materials will be albe to withstand the conditions of stress and thermal shock while at the same time effecting a hermetic seal. However, a decision should not be made until the preliminary investigations have been completed.

Details about these battery problem areas, and some of the approaches being taken to overcome these problems, are given in the main body of the report. The order of listing above is not meant to imply a measure of the severity of the problem.

Specific problem areas and research needs for fuel cells are listed below:

(A) In order to reach useful lifetimes of greater than 30,000 hours and commercially attractive costs of electricity for the solid electrolyte fuel cells, interconnection materials which are now life limiting must be vastly improved.

The major concern is compatibility of thermal expansion characteristics with other fuel cell components and their stability in air and fuel-gas.

(B) The high operating temperatures (1000 C) of the stabilized zirconia fuel cells present materials degradation problems and questions as to probable lifetimes. The use of alternate electrolytes and stack designs should be investigated. In particular, the more abundant and cheaper ceria compounds (gadolinia-ceria solid solutions) which offer the advantages of cell operation at 750 C and higher conductivities than stabilized zirconia, should be exploited. Lifetime problems should be less severe than at the 1000 C temperature and the lower resistivities might allow thicker electrolyte layers which could ease fabrication and enhance mechanical properties. The differences in thermal expansion properties of the ceria electrolytes would require that new substrate (tube or disk) and electrode and interconnector technology be developed to avoid problems such as the cracking in the zirconia cells caused by mismatch of expansion characteristics of the chromium sesquioxide. In general, more attention needs to be paid to the area of seals, feedthroughs and interconnection materials in the high temperature fuel cells in order to realize projected lifetime goals, since most of the research has been directed towards improvements in electrolyte conductivities.

(C) Since the molten carbonate fuel cell has been designated the prime candidate for the second generation fuel cell in utility applications, the problems of corrosion of construction materials needs to be solved. Another limitation on cell life is the sintering of the catalysts which reduces the active area and therefore cell performance. Cell lifetimes have usually been shortened by cracking of the paste supporting discs (MgO, Al_2O_3) allowing loss of electrolyte or mixing of fuel and air, or by corrosion of gaskets or the container materials.

(D) Since catalysts are needed for all but the high temperature fuel cells, reactive and less costly substitutes are needed to replace Pt-metal catalysts which at present are the only ones providing sufficiently rapid reactions. Reducing particle size of the noble metal increases surface area, activity, and can bring about a reduction in volume loading and therefore electrode costs. However, such particles are not stable in hot phosphoric acid fuel cells under electrolytic conditons. Sintering and agglomeration being a chief problem causes reduction in catalytic surface area and, therefore, cell performance. There is a strong need to replace the noble-metal catalysts with materials that are less costly such as ceramic oxides or carbides, which also must be good electronic conductors, stable at high oxidizing potentials in strong hot acid, and catalytically active. This last requirement might be difficult because for the fuel electrode it includes a lack of sensitivity to poisoning by CO and for the air electrode, a capability of reducing O_2 to OH^- and not HO_2^-. A number of electrocatalysts have been developed which show considerable promise such as lithiated NiO for alkaline fuel cells and tungsten carbide for acid cells. A continuing effort, however, is needed in the area of electrocatalysts, to bring about cost reductions and simultaneously improve performance and lifetimes.

Recommendations

Specific materials problems are being addressed on programs funded by government (ERDA, NASA, U.S. Army, USAF, etc.) by industry (Ford Motor Company; General Motors Corporation; Atomics International Division; United Technologies Corporation; General Electric Company, etc.) and by associations (EPRI). The objective of these programs usually is to develop a particular system for a selected application. There appears to be a definite need for two types of supportive efforts, involving both R and D and engineering development.

The first effort involves general studies to improve materials properties such as toughness and strength coupled with corrosion resistance (materials stability) in order that processing technology can be advanced to the stage that low cost products such as ceramic papers for separators, and powder with desirable rheological properties for the isostatic pressing of solid electrolyte components, can be prepared. Coupled with these studies would be related investigations such as improving ceramic processing technology so that high tolerance, homogeneous ceramic materials can be produced reproducibly at economically attractive costs to the battery manufacturers. Reject rates have to lowered when high volumes production processes are developed.

The second effort would be of a more theoretical nature and would address such problems as developing an understanding of structure/ionic conductivity relationships in solid electrolytes, and understanding the mechanism of corrosion attack on ceramic materials. The former could lead to microstructural control coupled with the desired physical, chemical, mechanical and electrochemical properties. Associated with the latter could be thermodynamic and electrochemical studies to determine the stability of ceramic oxide and nitride materials, for example. These data would then assist in the selection of engineering materials for the battery developers. A related area would be an extensive study on the effects of impurities on the performance of ceramic materials, along the line of the Cornell study[107] on beta-alumina. As engineering and eventually commercial cells are developed, and as operating temperatures are increased, impurities in the active materials, and resulting from degradation or corrosion of other materials, will be found in greater concentrations. It has already been shown that both cationic and anionic impurities qualitatively have a detrimental effect on many ceramic materials. A better understanding of the type of impurity likely to be found in a given cell internal environment, and its limiting concentration before cell performance or life is affected, is highly desirable.

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APPENDIX

LISTING OF BATTERY AND FUEL CELL SYSTEMS DISCUSSED IN THIS REPORT GIVING THEIR PERFORMANCE CHARACTERISTICS

TABLE A-1. PHYSICOCHEMICAL CHARACTERISTICS OF BATTERY SYSTEMS LISTED IN THIS REPORT

Battery System	Type[a]	Composition: Anode[b]	Composition: Electrolyte	Composition: Cathode	Principal Application(s)
			(1) Ambient Temperature Operation		
$Li-SOCl_2$	P	Li (s)	$LiALCl_4$	$SOCl_2$ (l)	Portable electronic devices
$Li-V_2O_5$	P,R	Li (s)	$LiASF_6 + LiBF_4$	V_2O_5 (s)	Munition systems
Zn-HgO	P,R,S	Zn (s)	KOH; NaOH	HgO (s)	Portable devices; electronic devices and instruments
Zn-AgO	P,R,S	Zn (s)	KOH	AgO (s)	Portable electronic devices and instruments
Zn-(Air)	P,S	Zn (s)	KOH	O_2 (g)	Portable devices; electronic devices and instruments
H_2-AgO	S	H_2 (g)	KOH	AgO (s)	Aerospace
$H_2-NiOOH$	S	H_2 (g)	KOH	NiOOH (s)	Aerospace
Cd-NiOOH	S	Cd (s)	KOH	NiOOH (s)	Aerospace; portable devices
$Pb-PbO_2$	S	Pb (s)	H_2SO_4	PbO_2 (s)	Portable devices; automotive; stand-by power
Na^*-Br_2	P	Na (s)	$\beta-Al_2O_3$	Br_2 (g)	Not determined
$Li-I_2$	P	Li (s)	LiI	I_2 (g)	Medical devices
			(2) Elevated Temperature Operation		
Na-S	S	Na (l)	$\beta-Al_2O_3$; glass	S (l)	Motive power and bulk energy storage
Na-MeCl	S	Na (l)	$\beta-Al_2O_3$	$SbCl_3$ (s)	Bulk energy storage
K-S	S	K (l)	glass	S (l)	Experimental
Li*-MeS	S	Li (s)	LiCl + KCl	{FeS (s) / FeS_2 (s)}	Motive power and bulk energy storage
Li^*-MeCl_2	S	Li (s)	LiCl + KCl	Cl_2 (g)	Motive power
$Li-Cl_2$	P,S	Li (l)	(LiCl + KCl)	Cl_2 (g)	Motive power
$Li^*-V_2O_5$	T	Li (s)	NaSCN + KSCN / LiCl + KCl	V_2O_5 (g)	Munition systems
Ca*-MeS	S	Ca (s)	$CaCl_2$ + LiCl + KCl	{FeS (s) / FeS_2 (s)}	Experimental
$Ca-CaCrO_4$	T	Ca (s)	$CaCl_2$ + LiCl + KCl	$CaCrO_4$ (s)	Emergency starting of vehicles; motive power
Na-Na	T	Na (l)	$\beta-Al_2O_3$	Na (l)	Experimental

* Alloyed to maintain electrode as solid at operating temperature.

(a) P = primary; S = secondary; R = reserve; T = thermal or thermoelectric.

(b) s = solid; l = liquid; g = gas.

TABLE A-2. PERFORMANCE CHARACTERISTICS OF BATTERY SYSTEMS LISTED IN THIS REPORT

Battery System	Operating Temperature,[a] F	Average Operating Voltage, V	Energy Density, w hr/lb	Power Density, w/lb	Maximum Reported Size Ahr	kw
$Li\text{-}SOCl_2$	0 - 150	2.80	100 - 150	--	(4000)[b]	(8)
$Li\text{-}V_2O_5$	0 - 150	3.20	29	--	0.5	0.001
Zn-HgO	60 - 150	1.30	30 - 35	30	--	--
Zn-AgO	0 - 150	1.40	45 - 70	40	300	1.0
Zn-(air)	0 - 150	1.30	30 - 55	30	200	27.0
$H_2\text{-}AgO$	0 - 150	1.10	30 - 50	30	500	--
$H_2\text{-}NiOOH$	0 - 150	1.25	15 - 25	25	55	0.01
Cd-NiOOH	0 - 150	1.10	15 - 25	--	1245	1.0
$Pb\text{-}PbO_2$	0 - 150	1.90	13 - 18	15	5000	2.5
$Na\text{-}Br_2$	70 - 120	3.50	100 - 170	--	--	--
$Li\text{-}I_2$	70 - 150	4.00	--	--	--	--
Na-S	540 - 750	1.84	45	48	700	1.0
Na-MeCl	300 - 460	3.00	45	45	5	1.0
K-S	500 - 750	2.00	--	--	--	--
Li-MeS	570 - 750	1.50	28 - 60	45	100	0.12
$Li\text{-}MeCl_2$	750 - 1200	3.00	38 - 60	50	30	--
$Li\text{-}Cl_2$	750 - 1020	3.45	80	60	--	0.65
$Li\text{-}V_2O_5$	~ 400	2.5	10 - 20	--	0.5	0.001
Ca-MeS	500 - 750	--	--	--	--	--
$Ca\text{-}CaCrO_4$	-65 - 200	2.3	5 - 20	--	3.0	0.23
Na-Na	500 - 750		--	--	--	--

(a) Nominal values, operation outside these ranges is often possible with a sacrifice in performance.

(b) Under development.

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A SURVEY OF THE USE OF CERAMICS IN BATTERY AND FUEL CELL APPLICATIONS
Eric W. Brooman, Keith R. Shillito and Walter K. Boyd, BATTELLE, Columbus Laboratories, Columbus, Ohio 43201

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Key Words

Battery
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Ceramic Materials
Solid Electrolytes

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